THE ANODIC OXIDATION
OF ALUMINIUM AND ITS ALLOYS

BY

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With 107 Illustrations and 36 Tables

International Book House,
Bombay.
LONDON:
CHARLES GRIFFIN AND COMPANY, LIMITED,
42 DRURY LANE, W.C. 2
1940

PREFACE

This monograph deals with the electrolytic and chemical production of protective surface films on aluminium and its alloys, and with their uses in practice. With the object of throwing light on the phenomena which occur in this comparatively limited field of surface treatment, considerable reference has been made to the production of rectifier valve films, the work on which has appreciably extended our knowledge relative to the production of protective films. The monograph does not deal with the processes of electroplating or metallic deposition on light metals, since this field has little in common with the subject treated.

The wide scientific and technical literature dealing with the light metals has increasingly drawn attention to the need for an effective corrosion protection for aluminium, and more particularly for its high-duty alloys which are of importance in engineering ; and a very large number of patents have been taken out in this connection. The number and extent of existing and newly erected plants for the production of anodic films are in themselves sufficient evidence of the technical interest and commercial importance of these protective films : and the need for the present monograph is accordingly apparent.

It is the object of the book to present in convenient form a general survey for the technically interested reader, who, in general, has not the time at his disposal to entertain a study of the extensive and scattered literature on the subject, with the object of making him rapidly acquainted with the present-day position in the field. For the benefit of readers not specially qualified in electrochemistry, an introductory study of the relevant electrochemical theory, without which understanding of the complex phenomena which occur is unattainable, has been given. No attempt has been made, however, to discuss the theory of the valve or rectifying effect, and reference is only made in passing to the conditions which obtain in this field, and which are extremely complex, since the phenomena are, for the most part, from a technical aspect fundamentally different from those concerned with surface treatment.

Anodic oxidation of aluminium and its alloys is, as the title indicates, the main theme of the book. Technically and commercially the anodic films rank in importance far ahead of the chemically produced protective films.

The treatise is divided into two main parts : In the General Part a survey of the electrochemical processes which form the subject of discussion is given, and an outline is also provided of the chemical behaviour of metals towards gases, and of the anodic phenomena at metallic electrodes. The General Section concludes with a chapter on the chemical properties of aluminium and its alloys, and on the electrolytic behaviour and anodic oxidation of aluminium, subdivided under direct-current, alternating-current, and combined-current treatments.

In the Special Section, the subject matter covers a general discussion on protective films, chemical phenomena at electrodes and in electrolytes, and the practical aspects of anodic treatment. An account is given of the commercial anodizing processes, and a chapter is also included on the chemical processes available for the production of protective films on aluminium and its alloys, with particular reference to the MBV process.

The original monograph, on which the present translation is based, formed one of the series of well-known *Technische Fortschrittsberichte* published by Theodor Steinkopff of Dresden and Leipzig—a well-chosen collection of treatises dealing with recent advances in specialist branches of science and technology. The author, Dr. A. Jenny, was Director of Research of the Siemens and Halske A.-G. Electrochemical Laboratories, and a foremost authority on the subject of anodic oxidation, to the researches on which he has contributed notably, perhaps his best-known work in this direction being his discovery and development of the use of oxide films on aluminium as a medium for permanent photography. Dr. Jenny has acknowledged his indebtedness to the Siemens and Halske Company for their permission to publish the results of much valuable research bearing on the subject matter, conducted in their laboratories.

Acknowledgments have also to be made here to The British Aluminium Company, Limited, for their kindness in allowing me to supplement the text with information gained from their Intelligence Department.

<div align="right">W.   LEWIS.</div>

April, 1940.

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OF

ALUMINIUM AND ITS ALLOYS

INTRODUCTION

ALUMINIUM occupies a special position, which it owes to its physical and chemical properties, among the light metals. It is the sole light metal which can be used in its elementary form as a constructional material.

F. Regelsberger defines as light metals those metallic elements whose specific gravity is less than 3·8.

A. von Zeerleder supports this differentiation from the heavy metals and applies it also to alloys, since the specific gravity of all

TABLE I.—LIGHT METAL ELEMENTS ARRANGED IN ORDER OF SPECIFIC GRAVITY

Name of Metal.	Chemical Symbol.	Specific Gravity at 20° C.	Atomic Weight.
Lithium	Li	0·534	6·940
Potassium	K	0·86	39·096
Sodium	Na	0·97	22·997
Rubidium	Rb	1·52	85·44
Calcium	Ca	1·54	40·08
Magnesium	Mg	1·74	24·32
Beryllium	Be	1·86	9·02
Caesium	Cs	1·87	132·91
Strontium	Sr	2·6	87·63
Aluminium	Al	2·69	26·97
Barium	Ba	3·7	137·36

the commercially important alloys which are embraced in practice in the term " light metals " also comes under this definition.

Among the aluminium alloys on the market, the highest specific gravity in the group of aluminium forging alloys is 2·8, and in the group of aluminium casting alloys the highest figure is 2·95 to 3·00. The proposed value of 3·8 as the upper limit for the specific gravity of the light metals therefore leaves an ample margin. It also embraces barium, as Table I shows: this element ranks, according to its position in the periodic system, among the alkaline earth metals,

and therefore properly belongs to the light metals ; whilst the rare earth metals, although chemically allied to aluminium, are excluded. This is the more rational since their technical application as constructional materials is out of the question, their utility being confined to other fields.

Under the title " light metals " are included, therefore, the alkali metals (lithium, sodium, potassium, rubidium, caesium), the alkaline earth metals (calcium, strontium, barium), magnesium, beryllium, aluminium and their alloys : and also the alloys of the light metal elements with heavy metals in so far as the specific gravity of 3·8 is not exceeded.

The fact that the elementary light metals were first isolated from their compounds, which had to some extent previously been known and used, in the 19th century, whilst the heavy metals, not including those precious metals found in Nature in the pure state, had already from dim antiquity been produced by some form of reduction process, is connected with the chemical resistance of the light metal compounds. The great affinity of these metals for oxygen is shown by the high heat of formation of their oxides. Whilst silver, which is an electronegative metal, exhibits a slight tendency to combine with oxygen, and only when finely divided and at an elevated temperature (300° C.) and an oxygen pressure of more than 15 atmospheres can be converted to oxide, the light metals which stand high in the electrochemical scale show a tendency even at ordinary temperatures to combine with the oxygen of the air to form oxides. For this reason it is difficult to liberate them from their oxygen compounds, and it is necessary to employ chemical or electrochemical processes involving large quantities of energy, which processes only became possible as chemistry and electro-technology were developed.

Table II shows the heats of formation of some metallic oxides. It indicates the affinity of the metals for oxygen, from which the energy required for reduction of the oxide can be gauged.

Aluminium, magnesium and calcium show the highest values for the heat liberated on oxide formation, the heat of formation of sodium oxide being considerably smaller, whilst the nearly equal values for potassium and zinc oxides follow at a considerable distance. The remaining oxides, those of the heavy metals, show values for the heat of formation which fall off continuously from iron to silver.

Corresponding to its high position in the electrochemical series zinc, whose oxide exhibits a comparatively high heat of formation, was not produced as a pure metal until recently. The European requirements for zinc had to be met by imports from the East Indies until well into the 18th century. Only then did the production of the pure metal commence in Europe. Among the

difficulties experienced in the production of this metal, which boils at about 910° C., were its volatility and its ready tendency to oxidize at the elevated temperature (1300° C.) necessary for its reduction.

Conditions were similar with the alkali metals, which are readily combustible and highly reactive to water. The fact that potassium, and later sodium, were first produced by the electrolysis of wet alkali hydroxide through the discovery of Davy in 1807 is to be explained less by the difficulty of reduction than by the previous absence of the necessary scientific knowledge and of a sufficiently developed technical background.

Once the alkali metals were isolated there was available a reducing agent more effective than anything previously known, with whose help it was possible to produce first aluminium, and

TABLE II.—HEATS OF FORMATION OF SOME METALLIC OXIDES
(taken from the *Landolt-Börnstein Physico-chemical Tables*)

Metal.	Specific Gravity at 20° C.	Metallic Oxide.	Molecular Weight of Oxide.	Molecular Heat of Formation, kg.-cals.
Silver . .	10·50	Ag_2O	231·76	+ 7·0
Mercury .	13·59 (0° C.)	HgO	216·6	+ 21·6
Copper . .	8·93	CuO	79·57	+ 38·5
Iron . .	7·86	FeO	71·84	+ 64·6
Zinc . .	7·12	ZnO	81·37	+ 83·3
Aluminium .	2·69	Al_2O_3 [1]	102·0	+393·3[1]
Magnesium .	1·74	MgO	40·08	+154·8
Calcium . .	1·54	CaO	56·08	+151·9
Sodium . .	0·97	Na_2O	40·0	+100·7
Potassium .	0·86	K_2O	56·09	+ 86·8

shortly afterwards, magnesium, in metallic form from their difficultly reducible compounds.

In 1825 H. C. Oersted succeeded in reducing aluminium by means of potassium amalgam. He obtained the aluminium in powder form. In 1827 F. Wöhler isolated aluminium from molten aluminium chloride, using potassium instead of the amalgam, and in 1845 he succeeded in producing the metal in the form of small lustrous globules. H. Sainte-Claire Deville started with the double chloride of aluminium and sodium. He carried out the reduction with sodium in the place of potassium, by which means the production was made cheaper.

Molten electrolysis was carried out almost simultaneously by Sainte-Claire Deville and R. Bunsen, who worked quite independently

[1] When the heat of formation of Al_2O_3 is divided by 3, *i.e.* when the value corresponding to ⅔ atom of aluminium and 1 atom of oxygen is obtained, it gives a figure comparable with that for the other oxides (131·1).

and in ignorance of each other's researches in 1854. They used the electric battery as a source of current. The economic production of aluminium was, however, first made possible by the development of cheap power, using a dynamo. P. L. T. Héroult in France, and Charles M. Hall in America, carried out researches in 1886 using a solution of alumina (aluminium oxide) in molten cryolite (sodium aluminium fluoride) for the electrolysis, and this process is still, to-day, the basis of commercial aluminium production. It was taken up by the Schweizerische Metallurgische Gesellschaft in Neuhausen in 1888 and was developed by Messrs. Kiliani and Héroult.
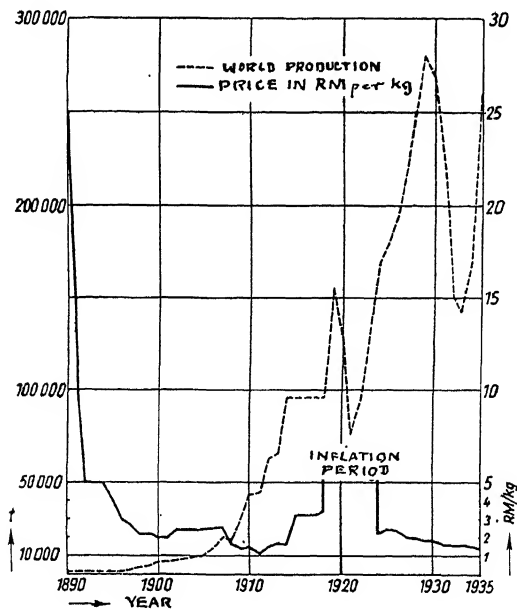
FIG. 1.—World Production and Price of Crude Aluminium.

Aluminium production in Germany to-day is carried out in several large aluminium reduction works. The chief of these is the Vereinigte Aluminium-Werke A.-G., which has its head office in Berlin and works in Lautawerk (Lausitz), Töging-am-Inn (Oberbayern) and Erftwerk in Grevenbroich (Niederrhein). Next comes the Aluminiumwerk G.m.b.H. of Bitterfeld and the Rheinfelden (Baden) Works of the Aluminium-Industrie A.G., Neuhausen. Having reached a peak consumption of 40,000 metric tons in 1929 the German consumption sank in 1932 to about 19,000 tons, and then rose again in 1933 to 28,000 tons, in 1934 to more than 52,000 tons, and in 1935 to 87,000 tons.

Table III presents a summary of the world production, world consumption and prices of aluminium ; and the way in which the price has fallen as the production has increased is shown in Fig. 1. The price of the metal during those years in which inflation occurred is not included, since it is meaningless.

TABLE III.—WORLD PRODUCTION AND WORLD CONSUMPTION OF ALUMINIUM

(in thousands of metric tons, according to F. Winteler and the Statistical Tables issued by the Metallgesellschaft, Frankfurt-am-Main)

(The prices are in RM. per kg. of Aluminium.)

Year.	Production.	Consumption.	Price.	Year.	Production.	Consumption.	Price.
1890	0·17	...	25·10	1914			1·65
1891	0·33	...	9·80	1915			3·25
1892	0·49	...	5·00	1916	96·7[3]	102·3[3]	3·25
1893	0·72	...	5·00	1917			3·25
1894	1·24	...	4·00	1918			3·42
1895	1·42	...	3·00	1919	156·0	156·1	(11·80)
1896	1·79	...	2·60	1920	127·7	131·9	(35·91)
1897	3·41	...	2·50	1921	75·6	71·3	(41·88)
1898	4·03	...	2·20	1922	92·8	100·1	(743·78)
1899	5·25	...	2·20	1923	139·1	140·3	...[2]
1900	7·31	...	2·00	1924	169·6	170·9	2·24
1901	6·95	...	2·00	1925	181·2	175·9	2·37
1902	...	...	2·40	1926	195·8	186·5	2·288
1903	...	...	2·40	1927	219·7	199·9	2·10
1904	9·3	9·3	2·40	1928	256·0	238·0	1·98
1905	11·5	11·5	3·50	1929	280·8	276·0	1·90
1906	14·5	14·5	3·50	1930	269·7	210·5	1·86
1907	19·8	14·8	3·60	1931	219·5	176·5	1·70
1908	18·6	17·0	1·65	1932	153·7	138·3	1·60
1909	31·2	35·3	1·40	1933	·142·0	158·4	1·60
1910	43·8	44·2	1·45	1934	170·8	227·0	1·57
1911	45·0	46·8	1·15	1935	259·2	306·6	1·44
1912	62·6[1]	69·9[1]	1·50	1936	366·5	407·4	1·44
1913	65·3	66·1	1·70				

Metallic aluminium as it comes from the reduction works is of different degrees of purity, and it finds its way to the market in three grades, 98-99, 99 and 99·5 per cent. purity. At the present time improvements in purity are being achieved and virgin aluminium of 99·7 per cent. purity is obtainable commercially.

Attempts completely to remove the impurities, principally iron and silicon, which are always present in aluminium, go back to the year 1900. In that year W. Hoopes took out an American Patent describing a process for the refinement of aluminium by molten

[1] The figures up to 1912 are estimated.
[2] Due to the Inflation, no estimate of the year's average is possible.
[3] Average for five years.

electrolysis. The technical difficulties in the way of this process condemned it to little success, but following Hoopes' idea A. G. Betts in 1905 brought out an improvement which was later to prove of fundamental importance for the subsequent development of aluminium refining. Betts introduced the three-layer system, in which the aluminium, containing heavy metals, which is to be purified, and which has the highest specific gravity, forms the undermost layer *A* (Fig. 2) and acts as anode. Above this layer comes a cryolite melt layer *B*, lower in specific gravity, which constitutes the electrolyte. The uppermost layer *C*, which has the lowest specific gravity, consists of the purified aluminium which forms the cathode. Seventeen years later, W. Hoopes, in collaboration with C. Frary and J. D. Edwards, was able to bring his researches
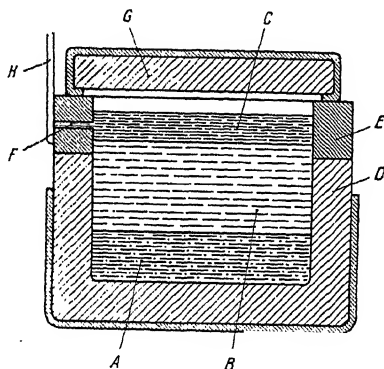
FIG. 2.—Refining of Aluminium in a Three-layer Cell.

A. Impure aluminium alloy.	*E.* Insulating refractory wall.
B. Electrolyte.	*F.* Space in wall for cathode
C. Cathode (pure aluminium).	current lead.
D. Carbon crucible (anode current lead).	*G.* Cover.
rent lead).	*H.* Cathode current lead.

to a satisfactory conclusion by making use of the three-layer system : and the principle is employed not only for refining aluminium, but also for the direct production of high-purity aluminium from the ordinary alumina-cryolite melt.

R. Gadeau has recently reported on the results obtained by the Compagnie d'Alais, Froges et Camargue using the Betts three-layer process. Until recently the purity obtained was 99·7 per cent. Al, but by using a specially purified alumina and petroleum coke anodes, aluminium of 99·85 per cent. purity could be obtained. It was not until 1922 that Hoopes succeeded for the first time in producing refined aluminium of 99·9 per cent. The French company referred to has recently developed a process by which aluminium of extremely high purity, viz. 99·99 per cent., and over, can be produced. The

electrolyte consists of a mixture of aluminium fluoride, sodium fluoride and barium chloride. The anode is an alloy of aluminium with 33 per cent. of copper. The refined metal contains :—

| Al | . | 99·992 per cent. | Si | 0·004 per cent. |
| Fe | . | 0·003 ,, ,, | Cu | 0·001 ,, ,, |

Some of the metal from the refining cells has even shown a purity of 99·998 per cent.[1] The physical and chemical properties of the super-purity metal differ markedly from those of the ordinary commercial aluminium, although the latter material only contains a few tenths per cent. of metallic impurities (principally iron and silicon, with traces of copper, zinc, titanium and sodium). The properties of super-purity aluminium, as compared with those of commerical aluminium and its alloys, are discussed elsewhere.

The low mechanical strength and, in many respects, the poor machining qualities of the ductile pure aluminium, soon led to a search for alloys which would meet better the requirements for a constructional material. Light alloys with excellent mechanical properties were early developed, but it was found that many alloying constituents had a deleterious influence on the resistance to corrosion. Later research was concerned with the abolition of this disadvantage. In this connection there are two lines of approach :

(1) The development of light alloys which have high mechanical strength and good machining qualities, whilst containing no constituents injurious to corrosion-resistance ; and

(2) The production of alloys which have maximum corrosion-resistance, more particularly in so far as sea-water is concerned, and with adequate mechanical properties.

Both categories of alloys embrace forging and casting alloys.

Among the innumerable varieties of alloys which were developed from these starting points, only a comparatively small, though by no means negligible, number have become of importance in practice. These alloys, which have now been in use for many years, have become indispensable construction materials in modern technology. Among them the copper-containing forging alloys of the Duralumin type are distinguished by their extremely high tensile strength and good mechanical properties. For the construction of heavily stressed components they have no rival, but in them, as in other alloys, the copper content has a very unfavourable effect on the corrosion-resistance. In order to provide a certain protection against corrosion without increase of weight and without sacrificing the original

[1] A. von Zeerleder and E. Zurbrügg give a detailed discussion of the development of aluminium refining, and of the results of researches by the Aluminium-Industrie A.-G., Neuhausen, in an article in *Aluminium*, **20**, 365, 1938.

good mechanical properties, it became necessary to seek new methods, since a protective paint which, to be effective, had to consist of several coats, hardly fulfilled the requirements. Research has produced two satisfactory solutions of the problem :

(1) Pure aluminium, which is more highly corrosion-resistant, or a corrosion-resistant aluminium alloy nearly equal in mechanical strength to the basis metal is plated (mechanically) on to the alloy.

(2) A non-metallic protective film is produced by chemical or electrochemical methods on the metal ; this film grows from the metal and is intimately rooted in it.

The second of these two processes depends upon the special property of aluminium and its alloys under appropriate conditions of oxidation to become coated with an oxide film which is firmly anchored to the basis metal and is very hard : and which, moreover, when given suitable treatment is almost completely resistant to corrosive atmospheric influences. Other metals, among which are numbered the magnesium alloys, exhibit a tendency to form similar coatings, but none among them produces surface films of such valuable properties, or with anything like equal protective effect, as aluminium.

This brings us to the subject matter proper of this monograph, which will now be fully discussed.

GENERAL PART

By chemically changing the surface of aluminium and its light alloys the following effects may be produced, either separately or in combination :

(1) Protection of the metallic surface against chemical attack or corrosion.

(2) Increase of the mechanical resistance of the surface.

(3) Permanent change of the surface appearance, which may be varied to suit any particular object.

(4) Electrical insulation.

(5) Valve effect, or rectifier effect.

Of these properties of the oxide films, the rectifier effect and the protective effect against chemical or mechanical influence are of special importance. Both from the point of view of historical development and technical importance, they are the focus about which the remaining properties are grouped.

The valve effect, or the rectifier effect, takes priority over all the phenomena which in the course of time have been observed in connection with aluminium anodes. For some fifty years it was the only property to attract the interest of scientific circles, before the knowledge obtained demonstrated its practical importance. It was only considerably later that attention was paid to the possibility of protection against chemical or mechanical action of the light metals, which were becoming important as constructional materials.

The fundamental difference between the rectifying effect and the protective effect is that an effective valve film, because of its small thickness, cannot exert an adequate protective effect ; whilst, conversely, a protective film which can, by reason of its porosity, be made of considerable thickness, is disqualified by this very thickness from being effective for use in rectifiers and condensers. It does not, therefore, follow that a rectifier film, or a film suitable for scientific investigation, necessarily possesses the requisite protective properties for technical applications.

The protective films may be produced by electrolytic or chemical processes, *i.e.* with or without the help of a source of electric current. In order to arrive at satisfactory results it is absolutely essential to have knowledge of the properties of the metal in question. In considering these properties, it seems desirable to differentiate between the chemical and electrochemical behaviour—corresponding to the two groups of processes—although metallic reactions in aqueous solutions, even where no external current is applied, are so closely connected with electrical phenomena that it is scarcely justifiable to distinguish between chemical and electrical processes. Nevertheless a separate treatment of the chemical behaviour in the above-defined sense is helpful, since it prepares the ground for a discussion of the electrolytic process ; for the chemical properties determine the electrolytic behaviour of the metal, and a knowledge of these properties is, therefore, essential to an understanding of the phenomena which occur during electrolysis. The physical properties will only be considered in so far as they influence the growth and the quality of the protective films ; and in the converse sense, when they refer to small changes in the mechanical properties of a metallic object due to oxidation treatment.

Compared with the chemical reactions which take place when metals are in contact with gases or with solid substances, the reactions which take place between metals and aqueous or molten electrolytes occupy a special place, in so far as in this case we are dealing with changes in substance between two electrical conductors of different kinds : the metal, in which the electrons are freely mobile (conductors of the first class), and the solution, in which electrical conduction takes place by way of ions (conductors of the second class). It is for this reason that the decompositions

which occur are coupled with definite electrical phenomena, an investigation of which is of especial importance in furthering our knowledge of the nature of chemical and electrical phenomena.

It seems desirable in the first instance, therefore, to consider quite generally the behaviour of metals towards aqueous electrolytes, before going into the question of the properties of aluminium, which, as has already been shown, possesses a quite remarkable affinity for oxygen, and whose reaction products, therefore, exhibit definite differences in properties from those of the commercially important heavy metals. Subsequently, a short section will be devoted to the reactions in gaseous media. The reactions of aluminium with substances normally solid at ordinary temperature are, if the behaviour towards mercury is excepted, of little importance technically, so long as no water is present. In the presence of moisture, however, the reactions which occur are in reality electrolytic. Processes for the production of protective films on aluminium in molten electrolytes have not been commercially developed and accordingly no discussion will be given of the phenomena which occur in these electrolytes.

CHAPTER I

PHENOMENA ACCOMPANYING THE DISSOLUTION OF SALTS IN WATER [1]

Solution Pressure : Osmotic Pressure

WHEN a salt is brought into contact with water it exhibits the property to a greater or lesser degree of going into solution. The force which brings about dissolution, namely the solution pressure, remains unchanged so long as any solid salt is present in the undissolved state, for the active mass, *i.e.* the spatial concentration of the solid salt, is constant. Another force, osmotic pressure, is opposed to the solution pressure and tends to make the salt re-crystallize from the solution, *i.e.* return to the solid form. At a given instant, when the solution is saturated, the osmotic pressure and the solution pressure are in equilibrium, *i.e.* equal amounts of salt go into solution and crystallize out. This dynamic equilibrium is changed the moment any variation in concentration cr in temperature of the solution occurs, for which energy has to be supplied. If the solution is heated up the solution pressure increases, and a further quantity of salt goes into solution. If the solvent is allowed to evaporate at constant temperature, the concentration increases, the osmotic pressure increases, and more salt crystallizes out than goes into solution.

When a salt dissolves in water there occurs yet another phenomenon which is of extreme importance in connection with our subsequent considerations. The electrically neutral salt splits up into electrically charged ions, that is to say, it dissociates in accordance, for example, with the equation :

$$NaCl \rightleftarrows Na\cdot + Cl'.$$

[1] This chapter is intended merely to give the reader not conversant with electrochemistry a general survey of electrochemical phenomena, and to familiarize him with the electrochemical terms which will occur frequently throughout the monograph. An exhaustive treatment of the subject is neither intended nor practicable within the limits of the present book. Readers are referred to the well-known works of W. Nernst, G. Grube and O. Bauer, O. Kröhnke and G. Masing for further information. In the last-mentioned authors' book will be found a discussion of the theory of corrosion. The present Chapter and Chapter II are based on these works of reference. Good books in English are J. Newton Friend's *A Text-book of Physical Chemistry*, 2 (London, 1935 ; C. Griffin & Co., Ltd., 24s.) and S. Glasstone's *Electrochemistry of Solutions* (2nd edition, London, 1938).

The solution of a substance which is partly or wholly dissociated into positive ($\cdot$) and negative ($'$) ions is termed an electrolyte. This definition is also extended to include the substance itself which splits up into ions in aqueous ·solution.

Degree of Dissociation

The degree of dissociation, *i.e.* the percentage proportion of the total dissolved molecules dissociated into their ions, depends on the concentration and to a very large extent on the nature of the dissolved electrolyte. Acids and bases, and even water, behave in the same way as salts. The degree of dissociation determines the electrical conductivity of the electrolyte, since only the ions can act as carriers of electric charges, whilst the charges on the ions joined to form undissociated molecules neutralize each other. The temperature has a comparatively small influence on electrolytic dissociation.

The salts of the alkali metals and of ammonium with monobasic acids undergo dissociation in dilute solutions of equivalent concentration to an equal and to a very large extent. The greatest differences in behaviour are found with the monobasic acids and with the monoacidic bases. Hydrochloric acid and caustic soda are as strongly dissociated as the above-named salts, whilst acetic acid and ammonia, even in dilute solutions, are split into their ions only to a very slight extent. Salts in which two ions each carrying a double electric charge are present, *i.e.* the salts of divalent bases and divalent acids, such as zinc sulphate and copper sulphate, are only about 25 per cent. dissociated in a 16 per cent. solution :

$$CuSO_4 \rightleftarrows Cu^{\cdot\cdot} + SO_4''.$$
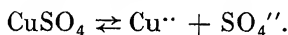
The behaviour of electrolytes which split up into more than two ions is different from the above. With an electrolyte of this type, such as sulphuric acid, which is of particular interest in connection with the subject-matter of this monograph, the dissociation into the SO_4 group with a double negative charge, and into the two hydrogen ions each with a single positive charge, does not occur directly but in two stages in accordance with the equations :

(1) $H_2SO_4 = HSO_4' + H^{\cdot}$; and
(2) $HSO_4' = SO_4'' + H^{\cdot}.$
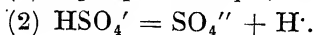
The same applies to pure water, which, as shown by its extremely small conductivity, possesses a very small degree of dissociation, the latter proceeding in accordance with the equations :

(3) $H_2O = H^{\cdot} + OH'$; and
(4) $OH' = O'' + H^{\cdot}.$
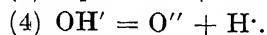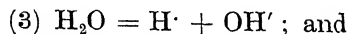
The second dissociation is much smaller than the first, so that water contains only an extremely small quantity of oxygen ions bearing a double negative charge. The degree of this second dissociation is not yet accurately known, but it can be assumed that oxygen ions are always present in water and in aqueous solutions. In accordance with equation (3) the concentrations of the hydrogen ions and of the hydroxyl ions in pure water are equal, and constant for a given temperature. The hydrogen ion concentration of pure water at 22° C. has been determined by different methods, which give good agreement, as 10^{-7} gram-ion per litre : this is equal to the hydroxyl ion concentration.[1] If we call these concentrations C_H. and $C_{OH'}$ it follows that

$$(5) \quad C_H. = C_{OH'} = 10^{-7} \text{ gram-ions.}$$

In accordance with the law of mass action there arises an equilibrium state in all reactions which do not reach completion, at which state the reaction stops of its own accord. This is true of the splitting up of water into its ions. The equilibrium state is reached when the concentration of the substances respectively being formed and disappearing reaches the particular constant ratio characteristic of the particular reaction. This means in the foregoing case that

$$(6) \quad \frac{C_H. \cdot C_{OH'}}{C_{H_2O}} = \text{Constant.}$$

This constant is called the *dissociation constant* (K).

Since the concentration of water (H_2O) in comparison with the extremely small concentration of its ions can be regarded as constant it follows that

$$(7) \quad C_H. \cdot C_{OH'} = K_w; \text{ or}$$

$$(8) \quad C_H. = \frac{K_w}{C_{OH'}} \text{ ; and in accordance with equation (5)}$$

$$(9) \quad C_H. = C_{OH'} = \sqrt{K_w}.$$

Equation (8) shows that the H· concentration is inversely proportional to the OH' concentration. Moreover, the product of the ionic concentrations in equation (7) is shown by equation (5) to be

$$(10) \quad C_H. \cdot C_{OH'} = 10^{-14}.$$

[1] One litre of H_2O therefore contains $1 . 10^{-7}$ g. of H· ions and $17 . 10^{-7}$ g. of OH' ions.

Phenomena of Neutralization : Hydrolysis

If pure water is acidified, *i.e.* if additional $H^{\cdot}$ ions from the acid are supplied to it (*cf.* equation (1)), the OH' ion concentration falls off in accordance with equation (7) or (8). Assuming $C_H.$ to be increased[1] to 10^{-3}, in accordance with equation (10) $C_{OH'} = 10^{-11}$, and

(11) $C_H. \cdot C_{OH'} = 10^{-3} \cdot 10^{-11} = 10^{-14}$.

Conversely $C_{OH'}$ increases and $C_H.$ decreases if alkali, *e.g.* caustic soda (NaOH), which splits up into $Na^{\cdot}$ and OH' ions, is added to the water. If equal quantities of $H^{\cdot}$ and OH' ions are added to the water, *i.e.* equivalent quantities of an acid and a base, the original concentration of the $H^{\cdot}$ and OH' ions does not change, and

$$NaOH + HCl = NaCl + H_2O, \text{ or}$$
$$Na^{\cdot} + OH' + H^{\cdot} + Cl' = Na^{\cdot} + Cl' + H_2O.$$
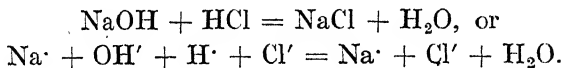
After taking away the ions common to both sides of the last equation there remains only the reaction :

$$OH' + H^{\cdot} = H_2O.$$
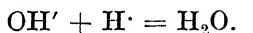
This means that the original concentration of the $H^{\cdot}$ and OH' ions in the water does not change during neutralization.

The process of neutralization sketched above presupposes that the dissociation constants (equation (6)) of the two reacting substances are large and approximately equal, that is to say, that a strong acid and a strong base, both of which are strongly dissociated in dilute solution, as is their reaction product, are both present. In the example given for the neutralization of NaOH by HCl this is the case. Combination to form NaCl does not here proceed to completion, *i.e.* it proceeds only until a certain equilibrium is reached, but the uncombined quantities of NaOH and HCl are vanishingly small and are no longer detectable. The reaction proceeds differently if one of the reacting substances has an extremely small dissociation constant, *e.g.* acetic acid. If this is made to react with an equivalent amount of NaOH the reaction product with the strong base has an alkaline reaction when the dilution is adequate (0·1 N.). This means that there are more OH' ions than $H^{\cdot}$ ions in the solution ; the dissolved sodium acetate is partly split up or *hydrolysed* into its initial constituents, acetic acid and sodium hydroxide, which behave as if they had taken no part in

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[1] The negative hydrogen exponent is designated by pH. In this case, *i.e.* in acid solution, pH = 3. In neutral solution (equation (5)) pH = 7 ; in alkaline solution pH is greater than 7.

the neutralization. Since the dissociation of the strong base is much greater than that of the weak acid, the solution reacts alkaline after the equilibrium state has been reached. Neutralization of a weak base by a strong acid proceeds in the same way, with the difference that the reaction product in this case exhibits an acid reaction.

A good example of hydrolysis is given by the neutralization of the tribasic orthophosphoric acid

$$P \begin{cases} = O \\ — OH \\ — OH \\ — OH \end{cases}$$
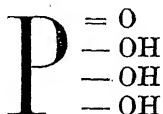
If to a dilute aqueous solution of phosphoric acid of known concentration methyl orange is added, this indicator shows the red coloration characteristic of an acid reaction. If now the quantity of sodium hydroxide required to neutralize one of the hydroxyl groups is added to this solution, it immediately gives rise to the formation of the monobasic phosphate NaH_2PO_4, and the colour of the methyl orange changes to yellow. This colour change occurs at a hydrogen-ion concentration of 10^{-4}. This shows that the monobasic sodium phosphate is almost completely dissociated into H_2PO_4'' and $Na\cdot$ ions, and only to a very small degree in accordance with the equation :

$$NaH_2PO_4 \rightleftarrows PO_4H' + Na\cdot + H\cdot.$$

If phenolphthalein is added to this solution, this indicator, which is colourless in acid solution, does not immediately turn red, since the solution does not react alkaline. The red coloration only appears when an additional quantity of sodium hydroxide sufficient to form the dibasic salt Na_2HPO_4 is added, and the commencement of the colour change of the phenolphthalein occurs at a hydrogen-ion concentration of 10^{-8} (*i.e.* $pH = 8$). This shows that the dibasic phosphate already reacts weakly alkaline, or that in this case hydrolysis has already set in, the reaction proceeding on the addition of the third gram-molecule of NaOH to 1 mol[1] of H_3PO_4 in accordance with the equation :

$$Na_3PO_4 + H_2O \rightleftarrows Na_2HPO_4 + NaOH \rightarrow Na_2HPO_4 + Na\cdot + OH'.$$
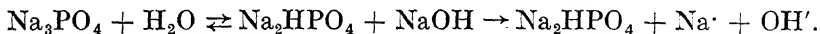
The degree of hydrolysis or the equilibrium constant of the hydrolytic decomposition can be calculated [2] from the dissociation

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[1] " Gram-molecule " is shortened to " mol ".

[2] For the derivation of the equilibrium constant of hydrolysis, *cf.* W. Nernst, *Theoretische Chemie*, Stuttgart, 1926 (5th English edition, London, 1923) ; see footnote on p. 11. See also J. Newton Friend, *A Text-book of Physical Chemistry*, **2**, 249 (London, 1935; C. Griffin & Co., Ltd., 24s.).

constants of the reacting molecules, which are characteristic of the strengths of the acids or bases in question.

Hydrolysis proceeds further if neutralization takes place between a weak base and a weak acid. In this case complete dissociation of the salt may occur if the base or the acid is difficultly soluble. Examples of such decomposition are supplied by the salts of the polyvalent metals with weak acids, such as the acetates of iron, aluminium, cobalt and nickel, which, because of the insolubility, or slight solubility, of their hydroxides tend even in moderately dilute solutions to exhibit extensive hydrolysis.

The following shows the degree of hydrolytic dissociation of salts of weak acids with strong bases. The figures refer to decinormal solutions at 25° C. :

Potassium cyanide, KCN	1·12 per cent.
Sodium carbonate, Na_2CO_3	3·17 ,, ,,
Potassium phenolate, C_6H_5OK	3·05 ,, ,,
Borax, $Na_2B_4O_7$	0·5 ,, ,,
Sodium acetate, CH_3COONa	0·008 ,, ,,

CHAPTER II

THE BEHAVIOUR OF METALS TOWARDS LIQUIDS

The Behaviour of Metals Towards Neutral Liquids

WHEN a metal is brought into contact with aqueous liquids, phenomena take place which can in many respects be compared with those which occur during the solution of salts in water. There is, however, a fundamental difference, which has already been referred to, because of the fact that reactions in which metals are concerned involve contact between two electric conductors, the metal and the electrolyte : whilst the solid salt, which dissolution of the metal may give rise to, is present as a non-conductor, in which case the electrolyte may not be effectively in contact with a conductor.

In accordance with Coehn's rule, substances of greater dielectric constant become positively charged when in contact with substances of smaller dielectric constant. From this it follows that metals, which are conductors of the first class, i.e. in which the electrons are freely mobile, acquire negative charges when in contact with dielectric liquids, such as paraffin, petroleum, etc., which are chemically inactive where metals are concerned, whilst the liquid becomes positively charged. Since this involves no material changes whatsoever the first stage is purely the taking up of static charges by the two substances in contact.

The Behaviour of Metals towards Aqueous Solutions

The conditions are quite different when we are dealing with aqueous solutions, which, as well as pure water, are, as we have seen, electrolytes. The sign of the charge may in this case, as will shortly be shown, be reversed as a result of electrochemical reactions which are determined by the nature of the metal and of the electrolyte. Coehn's rule is no longer generally applicable in the case where contact occurs between metal and electrolyte.

If a metal is immersed in pure distilled water it exhibits, according to its nature, a greater or lesser tendency to go into solution. In

the case of the alkali metals the reaction with water, which is accompanied by evolution of hydrogen, proceeds with extreme violence, the metals entering into solution to form hydroxides. These hydroxides are, as we saw, extensively dissociated into their ions

$$2Na + 2H_2O = 2NaOH + H_2 \rightleftarrows 2Na^. + 2OH' + H_2$$
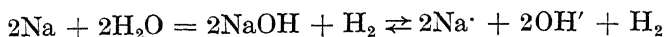
The alkaline earth metals, calcium, strontium and barium, react less violently with water, but in their case also, hydrogen is set free and the hydroxides go into solution. The reaction, however, proceeds considerably more slowly than with the alkali metals, because of the comparatively small solubility of the alkaline earth hydroxides. In the case of the heavy metals, the tendency to dissolve in pure water is very slight, since the reaction products are either completely insoluble or difficultly soluble : and analytically no dissolution at all is detectable with the noble metals. It must be assumed, nevertheless, that all metals possess a certain tendency to dissolve and have a definite solution pressure, even towards pure water. All the heavy metals become negatively charged when in contact with water, since water takes up a positive charge.

A vast amount of research has been carried out to investigate the behaviour of metals towards aqueous solutions. The chief interest is centred in the phenomena which occur in salt and acid solutions, whilst investigations regarding reactions in alkaline liquids are almost wholly confined to the behaviour of zinc and of aluminium. In this respect the alkali metals and alkaline earth metals, which react violently with water, are of less interest.

The heavy metals exhibit a tendency to go into solution in salt and acid solutions similar to that which, as we have shown, salts exhibit towards water. The dissolution of zinc in sulphuric acid, and of iron in hydrochloric acid, are well-known phenomena, as is also the process (made use of in metallurgy for the production of copper) in which iron, when immersed in copper sulphate solution, precipitates the copper on the iron, the latter going into solution. In these reactions, the same forces as those which we have recognized in the dissolution of salts play their part : solution pressure, the tendency of which is to make the metal go into solution, and the opposing force, osmotic pressure, which functions so as to make the metallic ions (which are always positively charged) leave the solution to re-join the metal. The dissolution of metals differs fundamentally from that of salts, however, in that the metal is capable of taking up electric charges whose electrostatic attraction for the oppositely charged ions of the solution may exert a condenser effect.

Behaviour of Metals towards Neutral Salt Solutions: Electrode Potential

If we consider the different possibilities of electrical charging which can arise when a metal is immersed in an aqueous neutral solution of one of its salts, as shown in Figs. 3 to 5, and if we denote the solution pressure by P, and the osmotic pressure by p, three cases are seen to be possible on the assumption that there are no disturbing side reactions at the metal/electrolyte interface :

1. If the solution pressure P is greater than the osmotic pressure p, the metal goes into solution with the loss of positive ions, while it itself becomes negatively charged. A second force, that of electrical attraction between the positive ions and the negatively charged metal, now opposes itself to the osmotic pressure (Fig. 3). An electrical double layer, in which the charges of opposite ions are opposed in the same way as in a charged condenser, forms in the
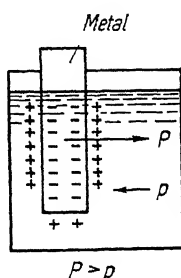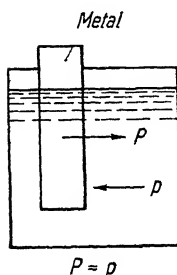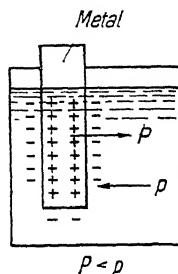
FIGS. 3-5.—Solution Pressure and Osmotic Pressure (diagrammatic).

neighbourhood of the metal/electrolyte boundary surface. As soon as equilibrium is reached between the opposing forces no further metal goes into solution. The quantity of metal which is taken up by the solution of one of its salts is too small to be measurable, but it is sufficient to give the metal its negative charge. The potential difference between metal and solution is defined as the potential of the metal towards the solution. The magnitude of the difference between P and p determines the magnitude of the potential difference, and the relative magnitude of P and p determines the sign of the potential, in this case negative since $P > p$. Let us assume that the reaction is taking place between zinc and zinc sulphate solution ; the phenomenon proceeds as follows :

$$Zn \rightarrow Zn^{\cdot\cdot} + 2e,$$
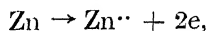
which means that one zinc atom when it goes over to the solution gives up two electrons (e) to the zinc, whilst it itself acquires a positive charge.

2. If we turn to the case shown in Fig. 5, in which $P < p$, *i.e.* in which the osmotic pressure of the ions is greater than the solution pressure of the metal, positive ions will separate one by one on the metal, which in consequence will assume a positive charge, whilst the negative ions of the acid electrostatically attracted will impart a negative charge to the liquid in the immediate neighbourhood of the metal. In this way an electrical double layer will again be formed, and an equilibrium state will ensue which will serve to prevent further emergence of positive ions from the solution. The metal will have a positive potential towards the solution. This behaviour may be observed when electronegative metals are immersed in solutions of their salts : as is known, the tendency of these metals to go into solution is very small, whilst they are readily precipitated from their solutions. The phenomena which occur may be illustrated by the example of copper in copper sulphate solution, where the following occurs :

$$Cu^{\cdot\cdot} + 2e \rightleftharpoons Cu.$$
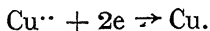
Expressed in words, the positive copper ion takes up two electrons from the metal, whilst it itself precipitates on the metal, which is equivalent to a diminution of the electrons in the metal and the acquisition of a positive charge.

3. In the third theoretically possible case, illustrated in Fig. 4, in which $P = p$, there is, in the same way as with a saturated salt solution in the presence of the solid substance, a dynamic equilibrium, in which an amount of metal equivalent to the ions which separate goes into solution. The potential of the metal towards its salt solution is equal to zero. We shall return to a consideration of this case later.

Sign of the Electrode Potential

The same considerations apply in the cases of the establishment of potential just discussed as in the case of the dissolution of salts. In this case also, the solution pressure is constant so long as any undissolved metal is immersed in the solution, since the active mass of the metal, *i.e.* its concentration, remains unchanged, whilst the osmotic pressure either decreases or increases until equilibrium is reached. This balance between P and p occurs so rapidly, and so little material is involved in it, that it is quite impossible to follow the phenomena either with time, or quantitatively. The magnitude and sign of the potential are the only indications of the changes which have taken place. The electrical double layer which arises from the electrostatic attraction of the oppositely charged metal and ions itself indicates an equilibrium state which is the result of the balance reached between the initially different P and p. The nature of the charge, or the sign of the potential of the metal

towards the solution, is determined by the ratio $P : p$. If this ratio is > 1, *i.e.* if $P > p$, the sign, as we have seen, is negative, but if the ratio is < 1, *i.e.* if $P < p$, it is positive. In the equilibrium state $P = p$ so $P/p = 1$, and the potential is zero.

Nernst's Equation

W. Nernst[1] has shown that the quantitative relationships between P and the osmotic pressure p, when a metal undergoes transition to the ionic state, and the work done are comparable, so long as the phenomenon is reversible and takes place at constant temperature, with the relations obtaining with perfect gases during reversible and isothermal changes in volume. Starting from this point, Nernst derived the well-known formula which expresses the relationship between the potential (in volts) of a metal immersed in a dilute solution of its salt, the solution pressure P and the osmotic pressure p. Reduced to its simplest form Nernst's equation becomes :

$$(1) \qquad \varepsilon = \frac{0 \cdot 058}{n} \cdot \log \frac{P}{p}$$

in which n is the valency of the metallic ions in the solution. If $P > p$ the potential will be negative, as we have seen. In this case :

$$\varepsilon = - \frac{0 \cdot 058}{n} \log \frac{P}{p}$$

which is the same as

$$(2) \qquad \varepsilon = \frac{0 \cdot 058}{n} \log \frac{p}{P}$$

Now, there exists a simple relationship between the solution pressure, the osmotic pressure and the concentration. It has already been shown that the active mass or the concentration C of a given metal is constant. P is, therefore, merely dependent on the material and is constant for any given pure metal. Again, the osmotic pressure p is proportional to the ion concentration c expressed in gram-ions per litre. Accordingly, in equation (2) the ratio of the concentrations $\frac{c}{C}$ can be substituted for $\frac{p}{P}$:

$$(3) \qquad \varepsilon = \frac{0 \cdot 058}{n} \log \frac{c}{C} \, ;$$

and since C is constant (K) :

$$(4) \qquad \varepsilon = \frac{0 \cdot 058}{n} \log \frac{c}{K}$$

The sole variable in this expression is c. Hence, it follows that the potential for any given metal is dependent only on the logarithm

[1] *Cf.* footnote on p. 11.

of the concentration of metallic ions in the particular salt solution, and increases by only $0 \cdot 058$ volt when c is increased ten times, e.g. rises from $0 \cdot 1$ to 1. As the metal ion concentration c increases, ε becomes larger—in other words, the potential shifts towards more positive values : as c decreases it shifts towards more negative values. For an accurately defined concentration of metal ions, such as one gram-ion per litre of solution, there exists accordingly a definite potential known as the " normal electrode potential," which is given the symbol ε_0.

Fig. 5, in which $P < p$, applies also to those cases where, as in the production of precipitated copper, a metal is precipitated from its solution by a second metal. If, for example, zinc is immersed in a copper sulphate solution, the zinc, whose solution pressure is greater than that of copper, goes into solution, whilst the equivalent quantity of positive copper ions is precipitated in metallic form on the zinc. The metal (zinc + copper precipitate) takes up a positive charge, and the solution a negative charge.

Galvanic Cells : Potential Difference (E.M.F.)

If we suppose the arrangements shown in Figs. 3 and 5 to be combined in the well-known manner with a porous diaphragm to form a galvanic cell, the electrostatic charges on the boundary surfaces of the metals and the liquids are removed as soon as a conducting metallic connection is produced between the metals or electrodes, through which the circuit is closed. The metal with the greater solution pressure may then again go into solution, while the ions of the other electrolyte precipitate on the metal with the smaller solution pressure. In the Daniell cell, shown in Fig. 6 and made up of

POROUS DIAPHRAGM
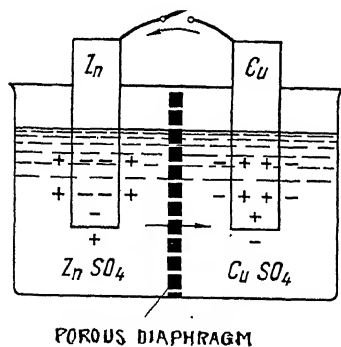
Fig. 6.—Galvanic Cell.

$$Zn/ZnSO_4 \text{ aq.}/CuSO_4 \text{ aq.}/Cu,$$
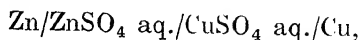
this potential balance takes place when a short circuit arises between the zinc and the copper. As long as the current flows, the electrons migrate in the external circuit from the zinc to the copper, and through the electrolyte from the copper to the zinc. The positive current, accordingly, flows in the opposite direction, shown in Fig. 6 by arrows. The electromotive force (E.M.F.) of the cell is given by the potential difference between the two electrodes. If

we denote the potential of the zinc by ε_{Zn}, and that of the copper by ε_{Cu}, the electromotive force is :

$$\text{E.M.F.} = \varepsilon_{Cu} - \varepsilon_{Zn}.$$

If we measure the E.M.F. of a cell in the known way with a voltmeter, we obtain invariably only the value of the difference between the actual potentials of the two electrodes. There is no method for determining with certainty the absolute value of the potential of a metal which is immersed in the solution of one of its salts. It is, therefore, necessary to arrive at relative values by measuring the potential difference between any desired metal immersed in the solution of one of its salts and a suitable reference electrode of constant potential.

Standard (Normal) Electrode Potential

Following on Nernst's proposal, the reference electrode chosen was the normal hydrogen electrode. This consists of a platinized electrode saturated with hydrogen gas immersed in a normal acid solution, *i.e.* a solution containing one gram-ion (equal to one gram-equivalent) of hydrogen per litre. Hydrogen is given up in large quantities from the platinized electrode, which accordingly behaves as if it consisted of metallic hydrogen. Taking the potential of the normal hydrogen electrode ε_{oH} as zero, any desired cell of the composition :

Metal/metal salt solution/N-H· solution/H_2(Pt)

gives directly the potential ε_{Me} of the metal against the given solution :

$$\varepsilon_{Me} - \varepsilon_{oH} = \varepsilon_{Me} - O = \varepsilon_{Me}.$$

If for this measurement the salt solution contains one gram-ion of the metal per litre, that is to say, if the cell consists of :

Metal/M-Me· solution/N-H·-solution/H_2(Pt),

the standard (normal) electrode potential of the metal on the normal hydrogen scale is obtained.

Measurement of Potential : Polarization

It is only possible to derive an accurate value for the potential if the cell has no current taken from it, for as soon as a current passes changes are produced at the electrodes and in the electrolyte which affect the true equilibrium state of the metal immersed in the solution. In order that the no-current condition may be arrived

at certain precautions have to be taken, which will not be entered into here.

Again, the true potentials will not be arrived at if the metal used in the determination has any impurities present in it. These impurities can occur in the form of inclusions which are present on the metal surface, or they may consist of chemical compounds, such as oxides, sulphides, etc., produced by the alteration which the metal surface undergoes on exposure to air.

The deviations of the potential values from the true equilibrium potential caused by such influences, more particularly those produced by current effects, are known as " polarization." The removal of polarization, *i.e.* depolarization, can be effected by different media known as depolarizers, but it is not invariably possible to undo the effects produced by polarization.

Electromotive Series

The carrying out of potential measurements accordingly demands meticulous observation of all the factors affecting the equilibrium condition. In many cases measurements are made more difficult by side reactions. If the metals tend to become passive, or if, as a consequence of hydrolysis setting in, any variation occurs in the metal ion content of the solution, the values obtained have some degree of uncertainty. Accordingly, the Electromotive Series (shown in Table IV), in which the metals are arranged in the order of their standard electrode potentials, gives only an approximate picture of the electrochemical character of the metals. Comparison with Table II shows that the heats of formation of the oxides increase approximately in the order of decreasing normal potentials of the metals.

The Electromotive Series gives accurate values for copper, zinc, lead and silver. In the case of the other metals the values must be regarded as more or less approximate. The figures will yield at the same time the decomposition voltages which require to be known for electrolysis. Table V extends the series of electrode potentials to include some anions.

From the standard electrode potentials the electromotive forces of galvanic cells of the type of the Daniell cell may readily be calculated. It may also be deduced from the Electromotive Series that iron will precipitate copper from copper solutions, and that where copper is immersed in a silver solution, silver will be precipitated on the copper. This frequently mentioned precipitation of a metal ion by a less noble metal is comparable with the reaction by which water is decomposed by metals with hydrogen evolution. Just as in the precipitation of copper, the solution pressure of the metal immersed in the water must also be very great in the case

of water decomposition, and the opposed osmotic pressure of the ions of this metal must be very small in comparison with that of the hydrogen ions. Sodium, with its extremely high solution

TABLE IV.—STANDARD ELECTRODE POTENTIALS OF THE METALS AGAINST HYDROGEN

Metal.	Chemical Symbol.	Ion.	ε_{oH}, volt.
Lithium	Li	Li·	−3·02
Barium	Ba	Ba··	−2·96
Potassium	K	K·	−2·925
Calcium	Ca	Ca··	−2·80
Sodium	Na	Na·	−2·715
Magnesium	Mg	Mg··	−1·8
Aluminium	Al	Al···	−1·337
Manganese	Mn	Mn··	−1·1
Zinc	Zn	Zn··	−0·76
Chromium	Cr	Cr··	−0·56
Cadmium	Cd	Cd··	−0·42
Iron	Fe	Fe··	−0·44
Cobalt	Co	Co··	−0·23
Nickel	Ni	Ni··	−0·20
Tin	Sn	Sn··	−0·146
Lead	Pb	Pb··	−0·132
Hydrogen (1 atm.)	H_2	2 H·	0·0
Antimony	Sb	Sb···	+0·2
Copper	Cu	Cu··	+0·347
Copper	Cu	Cu·	+0·52
Mercury	Hg	Hg_2··	+0·793
Silver	Ag	Ag·	+0·799
Platinum	Pt	Pt··	+0·86
Gold	Au	Au···	+1·38
Gold	Au	Au·	+1·5

TABLE V.—DISCHARGE POTENTIALS OF SOME ANIONS

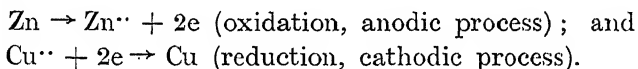|	Ion.	ε_{oH}, volt.
Oxygen (1 atm.)	O″	+1·23 [1]
Chlorine (1 atm.)	Cl′	+1·353
Hydroxyl	OH′	+1·68 [1]
Sulphuric acid	SO_4″	+1·9
Acetic acid	CH_3COO′	+2·5
Sulphuric acid	HSO_4′	+2·6

pressure, decomposes water with violence in all circumstances : its dissolution cannot in any case be prevented, since it is neither possible to render the osmotic pressure of the hydrogen ions small enough, nor to raise that of the sodium ions to a high enough value.

[1] The values for O and OH relate to a solution of normal hydrogen-ion concentration.

Zinc possesses a sufficient solution pressure to set hydrogen free in acid solutions, but the decomposition of the water stops as soon as the concentration of the zinc ions becomes large and that of the hydrogen ions becomes small, which conditions are fulfilled if zinc is immersed in neutral zinc sulphate solution. Copper gives rise to rapid evolution of hydrogen in potassium cyanide solution, since the copper ions form a complex salt $K[Cu(CN)_2]$ with the excess potassium cyanide. The formation of the complex anion removes, as it were, the copper ions from the solution. Resulting from the lack of copper ions in solution, the action of the solution pressure of the copper remains unchanged, whilst the osmotic pressure of the hydrogen ions becomes sufficiently great, in spite of the alkaline reaction of the solution,[1] to maintain a lively evolution of gas. This case is a typical one in which a side reaction has an accelerating effect on the solution of the metal and on hydrogen evolution. Later we shall have to concern ourselves with the converse phenomenon, in which a side reaction may inhibit or completely arrest the solution of a metal.

Dissolution of Metals

The foregoing considerations have shown that the reaction between metals and their aqueous salt solutions is a definite electro-chemical phenomenon. Regarded chemically, the phenomenon is nothing other than an oxidation and reduction reaction affecting the metal immersed in the solution, which can be expressed by the equations :

$$Zn \rightarrow Zn^{\cdot\cdot} + 2e \text{ (oxidation, anodic process)}; \text{ and}$$
$$Cu^{\cdot\cdot} + 2e \rightarrow Cu \text{ (reduction, cathodic process).}$$

In the cases of the dissolution of sodium in water to give sodium hydroxide, and of zinc in sulphuric acid to give zinc sulphate, hydrogen is set free. The metal in contact with the water or the sulphuric acid, therefore, behaves on the one hand as if it were an anode in a circuit fed from an external source of current, and on the other hand it behaves as a cathode, since hydrogen is evolved at it. If zinc is immersed in a copper sulphate solution it takes on a similar double rôle : on the one hand it brings about copper deposition as if it were the cathode during electrolysis, and on the other hand it goes into solution, which is equivalent to an anodic or oxidation process. The behaviour of zinc in sulphuric acid differs from that of zinc in copper sulphate only in that hydrogen is set free in the first case, whilst copper is precipitated in the second case. There is apparently no fundamental difference. In both

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[1] In aqueous solutions the hydrogen-ion concentration is approximately inversely proportional to the concentration of the hydroxyl ions (cf. p. 13, equation (8)).

cases a readily soluble zinc sulphate is formed, which is in the first case accompanied by hydrogen evolution, and in the second by deposition of copper. If, however, the investigation is repeated with high-purity zinc instead of ordinary commercial zinc, no hydrogen evolution will be observed. Although zinc has, according to the Electromotive Series, a far greater solution pressure than hydrogen, the charged hydrogen atoms adhere to the metal surface. Their combination to form molecular hydrogen, H_2, and to give rise to the evolution of gaseous hydrogen is frequently almost completely inhibited. If the zinc rod is now put in contact with a wire of a more electronegative metal, such as copper or silver, the gas evolution momentarily occurs whilst the zinc goes into solution ; the same is observed if a few drops of copper sulphate or silver nitrate are added to the diluted acid. As we have seen, in this case a small quantity of the more electronegative metal precipitates on the zinc. The addition of the salt of a more electronegative metal has, therefore, the same effect as actual contact with the more electronegative metal.

Accordingly, two conditions are responsible for the behaviour of pure zinc in dilute sulphuric acid :

(1) The absence of impurities with a more positive electrode potential.

(2) The covering of the metal surface with atomic hydrogen, which imparts to the zinc the more positive potential of the hydrogen and inhibits its solution. No combination of the hydrogen atoms to form molecules of gaseous hydrogen can occur under these conditions.

The origin of the causes which interfere with the combination of the hydrogen atoms to form molecules is not fully understood, but it is at least certain that this behaviour is closely connected with the phenomenon of overvoltage, which will be discussed later.

Local Elements

The relation between the course of the reaction and the degree of purity of the metal or acid has been explained by the theory of local currents or local elements which A. de la Rive put forward. According to this theory—provided the alkali metals, which react violently with water, are excluded—the attack of metals by aqueous solutions is accelerated if substances of different potentials or different solution pressures are present on the metal surface. The investigations already described with zinc and sulphuric acid provide an example : contact of pure zinc with a copper wire ; deposition of copper by adding zinc to a copper sulphate solution ; use of commercial zinc, which contains small quantities of copper, iron,

lead and arsenic. These three cases correspond to an arrangement in which two metals, in this case zinc and copper, for example, are immersed in acid and short-circuited, giving rise to a current-conducting circuit either inside or outside the acid. The more electropositive metal (zinc) goes into solution, whilst hydrogen is evolved at the more electronegative metal (copper). The conditions, which are shown diagrammatically in Figs. 7 and 8, can readily be understood from what has been said. The copper short-circuited with the zinc forms a galvanic cell in the acid. The zinc continuously goes into solution, the positive current flowing in the electrolyte from the zinc to the copper. The apparent contradiction that an oxidation and a reduction process, or an anodic and a cathodic reaction, are taking place simultaneously at the zinc immersed in the sulphuric acid is accordingly explained.
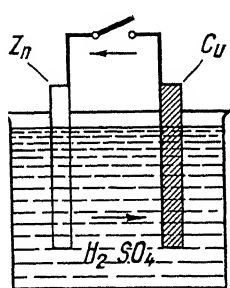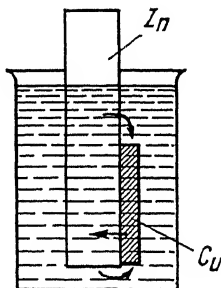
Fig. 7.   Fig. 8.

Figs. 7 and 8.—Local Elements (diagrammatic). (The direction of the current is indicated by arrows.)

The difference between the behaviour of pure zinc and zinc intentionally or unintentionally in combination with impurities (metallic) applies also to other metals, according to the theory of local elements. Depending on the nature of the metals in question, and on the metallic impurities present, the effect of the presence of local elements may make itself felt to a greater or lesser extent, and in a positive or negative direction, i.e. it may accelerate or inhibit the solution process, i.e. corrosion. If we assume, as we have done up to the present, that the decomposition occurring in the local elements gives rise to soluble reaction products, and if we regard the process purely from the electrochemical aspect, we arrive at the conclusion that the corrosion-resistance of the principal metal present is diminished by the presence of more electronegative constituents, and is increased by the presence of more electropositive constituents. In the majority of cases, however, the conditions which obtain are much more complicated.

Widely different impurities may reach the surface of an pure metal during mechanical working.
either good electrical conductors, such as metals
and crystalline silicon, or conductors of a lower
heavy metal oxides and sulphides. Finally, they may
of bad conductors or non-conductors, such as the oxides of the electropositive metals or other unintentional impurities. Any of these can affect the electrochemical equilibrium of the metal in question in a given electrolyte, and contribute to a greater or lesser extent to the formation of local elements.

In the following chapters we shall consider other factors which further or interfere with the formation of local elements, such as concentration differences in the electrolyte, unequal aeration, or the formation of surface films. At this point we shall only refer to some examples of surface films which have a corrosion-inhibiting effect, and which can form at the less noble constituent of an alloy acting as an anode : such examples are the chromium-containing stainless steels and May's brass, which contains about 2 per cent. of aluminium. In both cases the protection from corrosion is brought about by the fact that the less electronegative alloy constituents—chromium and aluminium—corresponding to their position in the Electromotive Series (*cf.* Table IV) become covered with a coherent dense oxide film which arrests, or extensively inhibits, the local element action.

Homogeneous and Heterogeneous Alloys : Resistance Limits[1]

The foregoing considerations of the behaviour of alloys towards aqueous solutions have merely shown that the difference in potential between the alloy constituents conduces to the formation of local elements which may delay or completely prevent the equilibrium state between metal and electrolyte being arrived at. The influence which the quantitative proportion or degree of dispersion of the constituents exerts on the solution process has not been taken into consideration.

It is, of course, obvious that an alloy consisting predominantly of an electropositive metal with very small quantities of a more electronegative constituent, provides the best conditions for the existence of local currents. The converse case, in which the electronegative metal is the chief constituent is, however, not so easily dismissed, since it would appear that in this case a protective effect might be exerted by the quantitatively predominant more electronegative metal. These conditions have been explained by the researches of G. Tammann. Tammann differentiates between the homogeneous alloys which consist of a single crystal variety (solid solution), and heterogeneous alloys, which are composed of

[1] Taken from G. Masing, see footnote on p. 11.

two or more crystal varieties. In the latter intermetallic compounds may also be present among the grains.

Chemical attack on a homogeneous alloy may take place in two ways :

(1) The attacking medium only attacks the more electropositive constituent, whilst the more electronegative metal remains unchanged.

(2) The attacking medium attacks both alloy constituents.

Tammann investigated the first case and demonstrated that attack of the more electropositive metal only occurs when the ratio of the number of atoms of the more electronegative metal to the number of atoms of the alloy falls below a certain limiting value. If
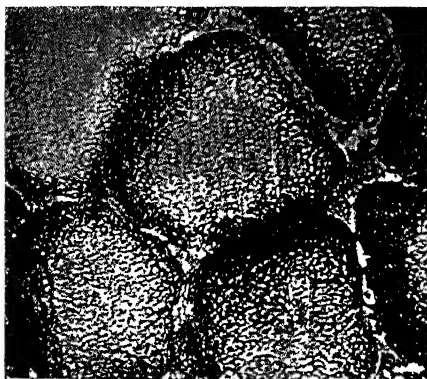
Fig. 9.—Zonal Solid Solution ($\times 500$). (After V. Fuss.)

this limiting value, which Tammann named the resistance limit, is exceeded—in other words, if the number of atoms of the more electronegative metal rises above the resistance limit—the chemical medium will no longer attack the more electropositive metal. Above this limit, the more electronegative metal exerts a protective effect. Among alloys the resistance limit is never higher than 50 atomic per cent. of the more electronegative constituent.

The conditions are otherwise if both alloy constituents are attacked by the chemical medium, which is in practice by far the most frequently occurring case, and applies invariably to the commercial alloys of aluminium with which we are concerned. In this case there is no longer a resistance limit. The solution process is again, in this instance, accelerated by a small content of electronegative metal, and will proceed most rapidly when the maximum number of *isolated* single atoms of the electronegative metal are

uniformly distributed throughout the electropositive metal, which can only arise when the electronegative metal has undergone a certain dilution.

In practice, a completely uniform distribution of the constituents of a solid solution hardly ever occurs, because of the occurrence of the phenomenon known as crystal or grain segregation. Fig. 9 shows the zonal appearance of the solid solution brought about by enrichment of one constituent at the grain boundaries.

In the case of the heterogeneous alloys, which consist of two or more crystal varieties, the conditions necessary for the formation of local elements are present *ab initio*. Such alloys are not attacked only if all the crystal varieties considered separately lie above the resistance limit and if one constituent is insoluble.

It follows that the heterogeneous alloys do not differ fundamentally in their electrochemical behaviour from the homogeneous alloys which contain a small quantity of a more electronegative constituent. With both alloy types surface films may be formed, however, and these may influence the progress of the attack and in some circumstances prevent it. It is important in connection with the considerations with which we are concerned to bear in mind the fact that the constituents of solid solutions, and also those of intermetallic compounds, can behave as local elements.

Concentration Cell

It has been earlier shown that the measurement of the potential can only give accurate values if no current passes through the electrode. Let us now consider the electrochemical cell shown in Fig. 10, which is made up as follows :

$$Zn/2N\text{-}ZnSO_4 \text{ solution}/0 \cdot 1N\text{-}CuSO_4 \text{ solution}/Cu.$$
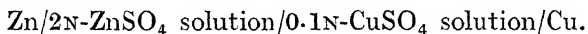
Once the circuit is closed, variations in concentration occur in the neighbourhood of the electrodes. The zinc, as anode, goes into solution ; the concentration of the zinc sulphate in its immediate neighbourhood is increased, whilst dilution of the electrolyte occurs at the copper cathode due to the deposition of copper and to the migration of the anions. The magnitude of the concentration variations depends on the current density and on the rate of diffusion in the electrolyte, and results in a shift of the potentials of the electrodes.

A concentration cell may be formed if the cell shown in Fig. 10 is made up with two zinc electrodes in zinc sulphate solutions of different concentrations, *i.e.* :

$$Zn/2N\text{-}ZnSO_4 \text{ solution}/0 \cdot 1N\text{-}ZnSO_4 \text{ solution}/Zn.$$
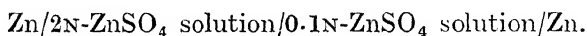
When the circuit is closed, the current flows in the electrolyte from right to left, since the zinc has a more negative potential in the dilute solution than in the concentrated solution.

Oxygen Concentration Cell

If the vessel shown in Fig. 10 is filled on both sides with the same electrolyte, and if the electrodes are of the same material, it is possible to form a cell by conducting oxygen or air through the electrolyte on one side. When the circuit is closed, a current flows in this case in the electrolyte from the non-aerated electrode, which behaves as anode, to the aerated cathode. This means that aeration has the effect of making the potential more positive. U. R. Evans was the first to point this out, and he further showed that even on a sheet immersed vertically in an electrolyte local currents were produced, due to the fact that the sheet at different levels was exposed to different quantities of oxygen.
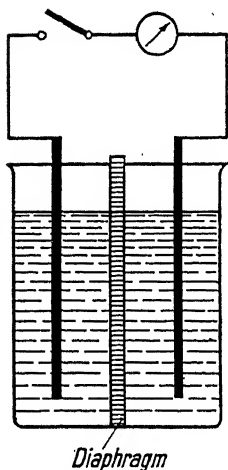
Due to differential aeration, in the first place an oxygen concentration cell is formed, and, further, chemical decomposition occurs at the electrodes. At the cathode, which is the aerated electrode, the oxygen is reduced by the hydrogen to form water: $2H\cdot + O + 2e = H_2O$, whilst oxidation of the hydroxyl ions proceeds at the non-aerated anode to form oxygen: $2OH' = H_2O + O + 2e$.

Diaphragm

Fig. 10.—Concentration Cell.

We shall shortly return to these phenomena.

Dissolution of Pure Metals by Acids

In the case of pure metals the difference of potential between the metal and hydrogen determines their dissolution in acids, and the hydrogen evolution which this involves. If the potential of the metal is more positive than that of hydrogen in the same acid, no solution will take place. In the other case, when the potential of the metal is the more negative, the metal will dissolve with evolution of hydrogen. This applies, as in all cases, only if disturbing side reactions do not give rise to polarization. If polarization phenomena do not arise while an electropositive metal is going into solution, its potential will increase as the concentration of its ions in the electrolyte increases until the value of the particular hydrogen potential is reached, this value becoming more negative as the acid becomes progressively neutralized and as the hydrogen-ion

concentration becomes diminished. The dissolution process may in consequence stop entirely. In the case of the commercial metals it is only rarely that they are available in such a pure form that the potential difference compared with hydrogen is the sole deciding factor. In almost all cases the presence of greater or lesser amounts of impurities and the consequent formation of local elements have to be reckoned with.

A Thiel and J. Eckell have shown that the purest available zinc (they used single crystals of the metal) is scarcely attacked even by hydrochloric acid. The same is true of high-purity iron.

Decomposition of Water by Metals

The evolution of hydrogen brought about by the alkali metals and the alkaline earth metals has already been briefly discussed. We are now in a position to give a more detailed account of the action of the heavy metals on the basis of what we have already discussed. Since water is split up into its ions, although only to a small extent, and has a hydrogen-ion concentration of 10^{-7}, a metal in contact with water must evolve hydrogen once the metal potential is lower than the potential of the hydrogen electrode. In the case of pure water, Nernst's formula gives: $7 \cdot 0 \times 0 \cdot 058 = -0 \cdot 406$ volt, a value close to the standard potential of iron ($-0 \cdot 44$ v.) and of cadmium ($-0 \cdot 42$ v.) (Table IV). Immediately after these metals are immersed in water, however, their ion concentration is vanishingly small, and accordingly, their potential in pure water is considerably more negative than it is in a molar solution of their ions, so that these metals initially evolve hydrogen rapidly, whilst the rate of evolution subsequently falls off. It may be observed as a fact that iron is capable of evolving small quantities of hydrogen in water and, provided air is excluded from the water, makes the latter react alkaline, since the resulting ferrous hydroxide is split up into $Fe^{..}$ and OH' ions. If atmospheric oxygen is present the reaction proceeds otherwise. The ferrous hydroxide becomes oxidized to ferric hydroxide; in the event of there being unequal aeration, local currents are formed, as we have shown.

Overvoltage of Hydrogen and Oxygen

It has been shown that when pure zinc is dissolved in dilute sulphuric acid, atomic hydrogen deposits on the metal without there being any visible gas evolution, i.e. the reaction:

$$2H^{.} + 2e = H_2$$
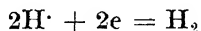
proceeds in the case of pure zinc with an extremely small velocity, which is in practice not detectable.

It has been observed in electrolysis that hydrogen evolution occurs at different cathode metals at different voltages. This means that the reaction by which the ions of hydrogen are converted at the cathode into molecules meets with a resistance of different magnitudes in the case of different metals. The mechanism of the whole phenomenon, which has several contributory processes, is not yet fully understood, although much research into it has been carried out. It is certain that there is a lag in the transition of the hydrogen ions present in the solution to the state of gaseous molecules, which lag is dependent on the nature of the electrode metal, on its surface condition, and to some extent also on the composition of the electrolyte. The greater the effective surface

TABLE VI

(According to H. Daneel)

Hydrogen Overvoltage.		Oxygen Overvoltage.	
Metal.	Potential, volts.	Metal.	Potential, volts.
Pt, platinized	0·00	Au	0·52
Au	0·02	Pt, smooth	0·44
Fe, in NaOH	0·08	Pd	0·42
Pt, polished	0·09	Cd	0·42
Ag	0·15	Ag	0·40
Ni	0·21	Pb	0·30
Cu	0·23	Cu	0·25
Pd	0·48	Fe	0·24
Sn	0·53	Pt, platinized	0·24
Pb	0·64	Co	0·13
Zn	0·70	Ni, bright	0·12
Hg	0·78	Ni, spongy	0·05

of the cathode, the smaller the lag. In the case of polished surfaces, therefore, the delay (for equal external dimensions) is greater than in the case of roughened surfaces.

The *minimum hydrogen overvoltage* of an electrode in a given solution is defined as the difference between the equilibrium hydrogen potential in that solution and the potential at which bubbles of hydrogen are just evolved. Platinized platinum cathodes require the smallest overvoltage to induce visible hydrogen evolution. In a similar way, oxygen overvoltages necessary to produce oxygen evolution at anodes of different metals may be determined, the values obtained being shown in Table VI.

This shows that the atomic hydrogen evolved when high-purity zinc is immersed in dilute sulphuric acid will be transformed into gaseous hydrogen only when a potential 0·7 volt more negative is

reached. This value is attained as soon as the zinc is put in contact with a copper wire.

The voltage between the two metals is 1·105 according to the Electromotive Series (Table IV). The hydrogen collected on the zinc can immediately come off as a gas, and the more electronegative copper now assumes the rôle of cathode, at which the hydrogen overvoltage is only 0·23v. With the voltage of 1·105 in the local element gas formation can occur without hindrance at the copper. This explains the part played by the hydrogen overvoltage in the solution of metals, and we are led to the conclusion, at least in the case of the example considered, that an absolutely pure heavy metal, in the absence of a more electronegative metal giving rise to a local element with a sufficiently great potential difference, cannot be dissolved by dilute sulphuric acid, or if at all dissolved the dissolution would proceed with extreme slowness.

If we consider further the conditions to which the hydrogen overvoltage gives rise, it is not difficult to discover some other factors affecting the solution phenomena in a local element. It is apparent that the dissolution of the basis metal will proceed the more readily the smaller the overvoltage of the more electronegative metal, *i.e.* of the metal behaving as the cathode. The dissolution will achieve its maximum velocity when the overvoltage becomes zero, that is to say, when platinum is employed as cathode. On the other hand, the dissolution will be brought to a standstill and hydrogen evolution will stop if the overvoltage at the surface of the basis metal is equal at all points or, in other words, if the basis metal is of such high purity as to render impossible any potential difference between different areas of the metal surface. If, however, such a potential difference is present, *i.e.* if a local element exists between two different metals, the potential difference between the metals will in general determine the dissolution of the baser metal. This will, however, as has already been mentioned, be influenced by the hydrogen overvoltage at the more electronegative metal, and may be completely arrested if the overvoltage reaches the value of the potential difference between the two metals.

Examples which throw light on these phenomena have been discussed by M. Straumanis in a recently published article. According to the Electromotive Series the potential difference in the zinc-tin cell is 0·76 − 0·15 = 0·61 v. The overvoltage of hydrogen on zinc is 0·70 v., and at the more electronegative tin is 0·53 v. The effectiveness of the local element will in this case, therefore, be very slight, since the potential difference (0·61 v.) only exceeds the overvoltage on the cathode (0·53 v.) by 0·08 v. In a second example, the zinc-lead cell, there is no effective action. In this case the potential difference is 0·76 − 0·13 = 0·63 v., and the overvoltage on the cathodic lead is 0·64 v. The potential difference and the overvoltage are

virtually equal. Hydrogen evolution at the lead and solution
of the zinc cannot occur, and no current flows through the local
element.

Shift of Potential due to Unequal Aeration

In the article referred to, Straumanis investigated the influence
of oxygen on the potential of the local cathodes. Starting from the
known fact that the overvoltage in air is smaller than in a hydrogen
atmosphere, that is to say, that the oxygen of the air shifts the
cathode potential to a more positive value, he discussed a further
possibility which the formation of non-homogeneous regions on the
metal surface gives rise to, namely, that of differential aeration.
In a well-known experiment he showed that local elements in the
presence of air and oxygen, as is the case with corrosion, exhibited
greater activity than in a hydrogen atmosphere. If a zinc plate
is connected to an iron plate through a sensitive ammeter and a
resistance, and if the plates are immersed in dilute sulphuric acid,
a current will flow through the cell, but the current density will
vary if the liquid is alternately saturated with hydrogen and oxygen.
In the electrolyte saturated with oxygen there is a greater potential
difference, and hence the current density developed is greater.
Measurements show that the variation of the potential occurs chiefly
at the cathode, that is to say, at the *locus* of hydrogen evolution.
Oxygen, therefore, actually tends to shift the potential of the local
cathode towards more positive values. Potential differences may
also arise, however, as has been shown, in accordance with Evans's
principle,[1] at a uniform metal surface where the oxygen access is
unequal.

In his researches Straumanis quantitatively investigated how the
potential of the cathode varies in relation to the oxygen access.
He employed platinum, nickel and carbonyl iron as his electronegative
metals and zinc in each case as the electropositive metal. The
electrolyte consisted of dilute sulphuric acid or hydrochloric acid
of different concentrations. The apparatus permitted of alternate
aeration of the cell with hydrogen, air or oxygen. Current density/
potential curves were determined for different current densities.

Fig. 11 shows the results obtained in the investigations with
platinum cathodes. The current density/potential curves were
derived from the potential values obtained in a number of series
of tests using different current densities. It can be seen that the
curves (4) for the zinc anode lie close together, since the potential
of the anode for a given current density is only slightly affected by
aeration with air, oxygen or hydrogen. As the current density
increases the potential shifts towards more positive values. On the

[1] *Cf.* p. 32.

other hand, the potential of the platinum cathode is to a large extent dependent on the nature of the gas present.   Curve 1 for platinum, obtained in a hydrogen atmosphere, represents nothing more than the overvoltage of hydrogen on platinum for different current densities, but the case is quite different with the potential curves for air and oxygen.   In an atmosphere of oxygen the potential of platinum reaches at +900 mv. almost the theoretical oxygen potential (+1·23 v.) for extremely small current densities, the
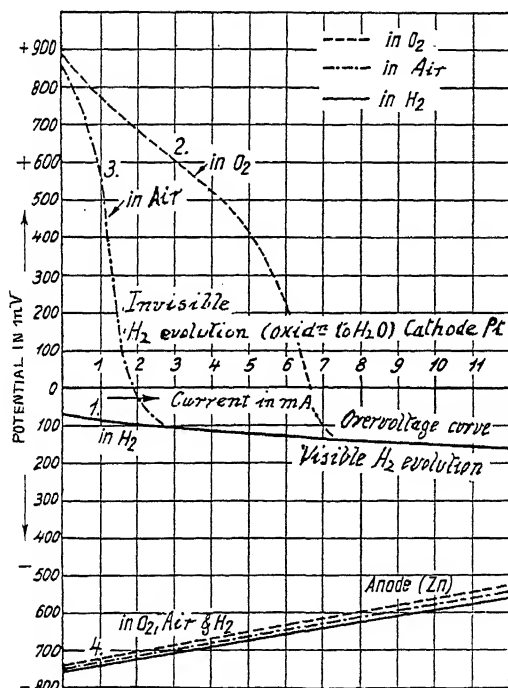
Fig. 11.[1]—Current Potential Curves of Platinized Platinum Cathodes and Zinc Anodes in Different Gases (Oxygen, Hydrogen and Air).   Cathode surface 4 cm.[2] ; electrolyte dilute sulphuric acid.   (After Straumanis.[1])

hydrogen evolution being actually invisible, since the discharged hydrogen is immediately oxidized to form water :

$$2H + O = H_2O.$$
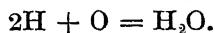
As the current density rises the potential becomes more negative, since adequate oxygen is no longer supplied by diffusion to the cathode.   The excess hydrogen is partly dissolved in the platinum, reducing the potential of the latter continuously until at about

[1] See p. 35.

7 mv. (current density 1·7 ma./cm.^{2}) the hydrogen potential is reached. Exactly similar phenomena are observed in the presence of air; but the depolarizing effect of the oxygen, in accordance with its small partial pressure, is smaller, as can be seen from Curve 3. It is also clear from Fig. 11 that the initial voltage of the cell, which is about 0·7 v. in a hydrogen atmosphere, is increased by aeration with oxygen to about 1·6 v., *i.e.* it is more than doubled. Phenomena of the same type are observed, although to a less extent, in the Ni/acid/Pt and Fe/acid/Pt cells. Various other depolarizers, such as potassium dichromate, potassium perchlorate, potassium chlorate and potassium iodate, when added to the electrolyte behave in exactly the same way as oxygen.

In connection with the matters under consideration, one result of these investigations is of particular interest, *viz.* the fact that the increase of the potential difference is solely attributable to the shift to more positive values of the potential of the cathode charged with hydrogen when oxygen is allowed access, whilst the potential of the anode remains almost unchanged. This shift to more positive values is explained by the acceleration of the reaction: $2H + O = H_2O$, and by the resulting diminution of the concentration of hydrogen at the cathode. The same explanation would apply to the potential differences arising in one and the same metal due to unequal aeration, as observed by Evans.

The foregoing considerations regarding the phenomena of the dissolution of metals have principally been confined to those metals and aqueous solutions which give rise to a readily soluble reaction product, whether it be a metallic salt, an alkali hydroxide or a similar product. The conditions vary markedly if the reaction product is insoluble, or difficultly soluble. The existence of an insoluble product may be either the consequence of a side reaction taking place in the electrolyte, as we have seen to be the case in hydrolysis, or the direct result of a reaction at the metal surface. In the latter case the phenomenon can give rise to the formation of a film covering the metal. This covering film may be either continuous and compact, or it may contain discontinuities, cracks and pores : it may be either a conductor or a non-conductor. These possibilities mean that the properties of such a surface film may determine the electrochemical behaviour of a metal.

It is hardly necessary to mention that such coatings may be formed in moist air. The phenomena of the rusting of iron and of the formation of verdigris on copper and copper-containing alloys are generally known. In discussing the chemical and the electrolytic behaviour of aluminium we shall have occasion to consider similar phenomena more closely.

The foregoing considerations have shown that the chemical reactions, that is to say, those which occur without the application

of an external source of current, between metals and aqueous solutions are connected in the most intimate manner with electrical phenomena. In fact no separation of the phenomena into chemical and electrochemical is possible. According to W. Palmaer, whose researches have contributed notably to the extension of our knowledge regarding local currents, there is no evidence of a simultaneous chemical attack.

CHAPTER III

THE CHEMICAL BEHAVIOUR OF METALS TOWARDS GASES

THE surface of a metal exposed to a gas comes more frequently into contact with the continuously moving gas molecules the higher the temperature of the gas. The gas in the immediate neighbourhood of a heated metal will act on the metal with increased energy as a consequence of the accelerated movement of its molecules. Again, the reaction will proceed with more vigour the greater the chemical affinity of the metal for the particular gas.

Atmospheric oxygen occupies the chief place of interest among the gases in connection with our considerations. In the present chapter we shall concern ourselves exclusively with it, and only later shall we consider the behaviour of other gases towards aluminium. What has already been said about the heat of formation of the metals has shown that the electronegative metals exhibit no affinity for oxygen, whilst the light metals have a very great affinity for oxygen, the commercially important heavy metals occupying an intermediate position. We shall consider the latter in the following.

Oxidation of the Commercial Heavy Metals in Air

In the case of oxidation, which is known to proceed to completion with divalent metals in accordance with the equation :

$$Me + O = MeO,$$
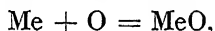
there is, in contrast to reactions between metals and aqueous solutions, no external electrical phenomenon to observe. The chemical valencies of the reacting substances are saturated in the newly created molecules. The oxide behaves as if it were electrically neutral, in so far as it receives no electric charge from the surroundings. Accordingly, oxidation in air, provided no moisture is present, differs fundamentally from the reactions in aqueous solutions. It must be regarded as a purely chemical phenomenon.

All the commercially used heavy metals oxidize to a greater or lesser extent, corresponding to their affinity for oxygen at ordinary temperatures. The oxide formed covers the metal with a surface film which hinders further attack by the oxygen and ultimately virtually stops such attack, since the gas molecules come less and less frequently into contact with the still uncovered portion of the

metal as the surface becomes progressively coated. It is presupposed that no water can condense on the metal, for if this were the case the reaction would be changed to an electrolytic one, and accordingly we assume that the reaction is taking place in air of ordinary humidity, rather less than that in an enclosed space. It has further to be supposed, for the purposes of our argument, that the reaction product, namely the oxide, is neither hygroscopic nor volatile. In the case of the commercial heavy metals these conditions apply in fact.

Once the coating of the metal with oxide is commenced the reaction velocity decreases, until the whole surface is covered with a more or less cohesive skin. Further reaction is then conditioned by the diffusion of the oxygen through the skin formed, which in turn depends on the nature and state of the metallic oxide. In the case of all the heavy metals and their alloys the reaction sooner or later reaches a standstill at ordinary temperatures provided no condensation of water occurs. The oxide film protects the metal from further attack.

H. Freundlich, G. Patschek and H. Zocher have demonstrated by optical methods the presence of an oxide film on high-purity iron mirrors produced *in vacuo* from iron carbonyl. Once the iron came into contact with oxygen its surface exhibited a changed optical behaviour towards reflected light compared with that shown in the initial state, which was unchanged by bringing the iron into contact with nitrogen or carbon dioxide (which, in contrast to oxygen, do not react with iron at ordinary temperatures). The same workers also showed that the solvent effect of nitric acid on iron previously exposed to oxygen became zero much sooner than with metal not so treated, since the oxygen had already taken a portion of the oxidation energy which otherwise would have been supplied to the nitric acid. The assumption that an oxide film is formed when iron is brought into contact with atmospheric oxygen may, therefore, be considered definitely proved, even though the film may be only a few molecules thick and invisible to the naked eye. R. Holm and his co-workers, in their investigations on the electrical conductivity of metals in contact, have shown that the commercial heavy metals do not, in air, possess pure metallic surfaces.

At elevated temperatures the reaction proceeds with much greater rapidity. The phenomenon is well-known in connection with the tarnishing which occurs when metals are heated. The proof that these tarnish films are in fact oxide films was supplied by U. R. Evans in his tests on nickel and iron rods. He showed, by dissolving the metal away from the skin formed, that the thickness of the oxide film increased as the temperature rose. Even when it was impossible with the naked eye to observe any variation of the metal surface he was able to show that a thin oxide film was present,

which curled up when the metal was dissolved ; this, moreover, provided a proof that there existed internal stresses in the film. The existence of a thin film on iron, nickel and copper could even be demonstrated if these metals had been exposed to air for any length of time at room temperature.

The internal stresses in the oxide film may lead to the formation of cracks, in which case oxygen diffusion takes place predominantly by way of the cracks. The further course of the reaction may also be influenced by the dimensions of the cracks and will proceed differently according to whether any cracks present are fine or coarse. Apart from the stress which may be present in the film, crack-formation depends on the mechanical properties of the film. A brittle oxide film will naturally have a greater tendency to crack than a flexible film. The nature of the metal surface will also exert an influence on the formation of the film : a chemically non-homogeneous or a rough surface will behave differently from a smooth homogeneous surface.

According to N. B. Pilling and R. Bedworth, the reaction between gas and metal will depend on the specific structure of the film which forms. If the surface of a wire is oxidized, a cylindrical metal surface will be replaced by a cylindrical oxide surface whose external diameter is determined by the first-formed oxide film. If the volume of the oxide is smaller than the volume of the metal it replaces, uncovered metal will remain behind the inner surface of the film, and the film will assume a cellular, porous structure. In the opposite case a homogeneous oxide film will be formed. The surface can freely expand outward, the extent depending solely on the coefficient of expansion. If the ratio

$$\frac{\text{Volume of oxide formed}}{\text{Volume of metal}} < 1$$

a porous film will be formed, and if the ratio is > 1 the film will be compact.

Table VII collates the values of this critical ratio of densities for different metals.

From this table it can be seen that the light metals give rise to porous films, whilst the heavy metals produce compact films. The oxide structure determines the extent to which oxygen penetrates to the metal surface. According to Pilling and Bedworth there are, however, exceptions to this rule, for example in the case of magnesium and of tungsten. In the case of the latter, the oxide which forms at 700° to 900° C. is in the form of a " spongy " powder which cannot exert any protection. In the case of calcium, the quantity of oxide formed at 300°, 400° and 500° C. is proportional to the time. Sodium and strontium are not protected from further attack by the film which forms on them. The appearance of temper

colours on metal surfaces, which is identical in origin with the
well-known phenomenon of the colours of thin films, has been used
by different research workers to determine the thickness of
electrolytically produced oxide films.   G. Tammann was the first
to undertake systematic observations of the temper colours in order
to determine a time law for the increase in thickness.   A. Günther-
schulze used the same method to determine the thickness of
electrolytically produced films on tantalum.   The laws discovered
by Tammann apply only to very thin films ; once the films grow
beyond a certain thickness, or if irregularities such as cracks occur
during their formation, the laws are no longer valid.   As far as our
knowledge goes, no satisfactory answer to all the questions concerning

TABLE VII

Metal.	Critical Density Ratio.	Metal.	Critical Density Ratio.
Al . .	1·28	Mn . .	2·07
Ba . .	0·78	Ni . .	1·68
Cd . .	1·32	K . .	0·51
Cs . .	0·42	Si . .	2·04
Ca . .	0·78	Na . .	0·32
Cr . .	3·92	Sr . .	0·69
Co . .	2·10	Th . .	1·36
Ca . .	1·70	Sn . .	1·33
Fe . .	2·06	W . .	3·30
Pb . .	1·31	Zn . .	1·59
Li . .	0·60	Zr . .	1·55
Mg . .	0·84		

reactions between gases and metals exists.   A great deal of
conjecture still has to be indulged in.

Passivity

If iron is immersed in hydrochloric, dilute nitric or sulphuric
acid, it readily dissolves with the liberation of a gas.   With con-
centrated nitric acid, however, the reaction does not take place.
Iron is only initially attacked by the concentrated acid, and the
reaction rapidly reaches a standstill.   This behaviour was early
observed and was given the designation " passivity."   The same
property was later discovered in connection with a number of other
metals, e.g. chromium, nickel and aluminium.   Faraday already
assumed that the passivity of iron was attributable to the formation
of an oxide film in the strongly oxidizing nitric acid.   As the above-
mentioned researches of Freundlich[1] and Evans[2] have shown, iron,

[1] Cf. p. 41.   [2] Cf. p. 41.

even when in contact with the oxygen of the air, becomes covered with a thin oxide film, not necessarily visible, which behaves as a passivating factor. A similar passivating effect to that exhibited by concentrated nitric acid may occur in dilute sulphuric acid to which is added a strong oxidizing agent, such as chromic acid. If the passivated iron is immersed in pure dilute sulphuric acid or in copper sulphate solution, there occurs neither hydrogen evolution nor copper deposition. The iron has acquired a more positive potential. If, however, the oxide film is removed by polishing with emery, the iron behaves again in the same way as it did before becoming passive, that is to say, it resumes its active character and regains its original potential.

The phenomenon of passivity is not necessarily bound up with the formation of an oxide surface film. The passive state may also be induced by other difficultly soluble compounds forming on the metal surface; thus it is possible to speak of the passivity of lead in sulphuric acid, a difficultly soluble film of lead sulphate being formed on the metal in this case.

CHAPTER IV

ANODIC PROCESSES AT METAL ELECTRODES DURING ELECTROLYSIS

IF a direct voltage is applied to two electrodes immersed in an electrolyte, there occur phenomena in the electrolyte and at the electrodes which are comprised in the general term " electrolysis." The course of electrolytic reactions is dependent on the nature and concentration of the electrolyte, on the nature of the electrodes, and on the applied voltage, which in turn determines the magnitude of the current and the density of the current at the electrodes. In the first instance we shall neglect the temperature of the solution and shall assume that this is maintained constant at 20° C.

Let us consider the simplest case, in which two electrodes of the same metal are immersed in a solution of a salt of that metal, *e.g.* two copper plates in a copper sulphate solution. From what has already been discussed we know that both electrodes possess the same potential, and that there exists no voltage between them. If we apply a small voltage of any desired magnitude to this cell by connecting one plate with the positive pole of a source of direct current, and the other plate with the negative pole, the ammeter will record the passage of a current, during which the plate connected as anode will send copper ions into solution, whilst metallic copper will deposit on the cathode. If provision is made for the prevention of concentration polarization, by keeping the solution stirred to achieve the maximum uniformity of concentration, a voltmeter connected across the cell immediately after the current has been switched off will show that there exists no potential between the electrodes.

Back E.M.F. or Polarization Voltage

If the experiment is carried out with the same copper sulphate solution, employing a smooth platinum plate as cathode, and a platinized plate as anode, it will be observed that a definite minimum voltage is necessary to maintain a measurable current. Since the platinum anode is insoluble in the electrolyte it takes up the oxygen

discharged at it, while copper still deposits on the cathode. We are now dealing with a cell of the constitution :

$$O_2/CuSO_4/Cu$$
$$\leftarrow$$
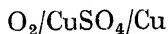
which boasts a definite terminal voltage ; this can be demonstrated by applying a voltmeter directly across the terminals of the electrodes immediately after the current is interrupted. The current then flows through the electrolyte in the direction of the arrow, from right to left, *i.e.* in the direction opposite to that of the applied current. During electrolysis, therefore, the E.M.F. of the cell is permanently opposed to that of the source of the applied current. This opposing E.M.F. is known as the *back E.M.F.* or *polarization voltage.*

Decomposition Voltage

The magnitude of the back E.M.F. depends on the phenomena occurring at the electrodes during electrolysis. In the case of unattackable electrodes it is always possible to demonstrate the existence of a polarization cell during electrolysis. The voltage which is necessary to overcome the opposing polarization voltage in order to permit current to pass is known as the *decomposition voltage* of the particular electrolyte. If the decomposition voltage is regulated so as to be equal to the polarization voltage, the current is equal to zero. M. Le Blanc has utilized this method for measuring the decomposition voltage in the polarization cell when no current is passing, and he has shown that at least the equilibrium potential of copper must be applied externally to a platinum cathode in order to bring about deposition on it of copper from normal copper sulphate solution ; and that chlorine is evolved from hydrochloric acid at a platinum anode only when the anode reaches the potential of the chlorine in the same solution. Accordingly the same relationships are found with electrolytic phenomena as with equilibrium potentials, providing the decomposition voltage is measured when electrolysis just begins.

Residual Current

If the voltage of the electrolytic cell is gradually increased the ammeter will be observed to show a rapid swing of the needle once the decomposition voltage is reached. If the current is plotted graphically against the voltage, a comparatively definite break occurs in the curve at the point corresponding to the decomposition voltage, at which point the current density suddenly increases (*cf.* Fig. 12). A small current, known as the *residual current*, flows even below the decomposition point. This is due to the fact that hydrogen and oxygen are formed at the electrodes in small amount,

and at low pressures, before the polarization voltage is exceeded by the applied voltage. These gases are dissolved by the electrolyte and do not, therefore, appear in the form of gas bubbles.

For the subject matter of the present monograph the phenomena which occur at metallic anodes are of particular interest to us. Cathodic metal deposition belongs to the fields of electroplating and electrometallurgy, which are outside the scope of our considerations. The same may be said of those processes in which other decomposition products arising during electrolysis are obtained. We shall concern ourselves with electrolytic oxidation and reduction, in so far as they give rise to variations in the concentration of the electrolyte,
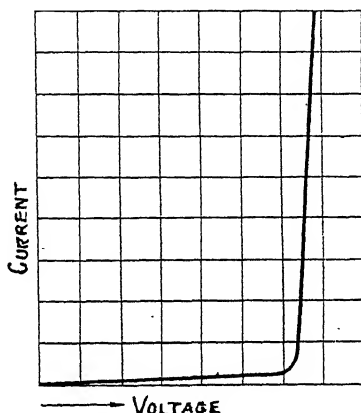
FIG. 12.—Residual Current below Decomposition Voltage.

in connection with our discussion of the phenomena of the anodic oxidation of aluminium.

Up to the present we have referred to only those cases in which the whole current is employed in sending a metal, such as copper, into solution, or in discharging ions at unattackable electrodes, such as platinum, which are not themselves dissolved. Those metals which on anodic polarization go into solution in different stages of valency, such as copper, iron and chromium, are of interest in connection with our subject matter only in so far as they give rise to surface films which provide an obstacle to the transference of ions of the metal into the solution, causing a considerable polarization and a more positive potential, and thus making possible the formation of ions of higher valency. The formation of anodic surface films, which oppose a considerable resistance to the current, can be observed also in the case of several metals which only go into solution in one valency stage. We shall become familiar with them in connection with the anodic oxidation of aluminium.

CHAPTER V

THE CHEMICAL PROPERTIES OF ALUMINIUM AND ITS ALLOYS

Oxidation in the Air

REFERENCE has already been made to the remarkable affinity of aluminium for oxygen, which finds expression in the high figure for the heat of formation of aluminium oxide (*cf.* Table II). To
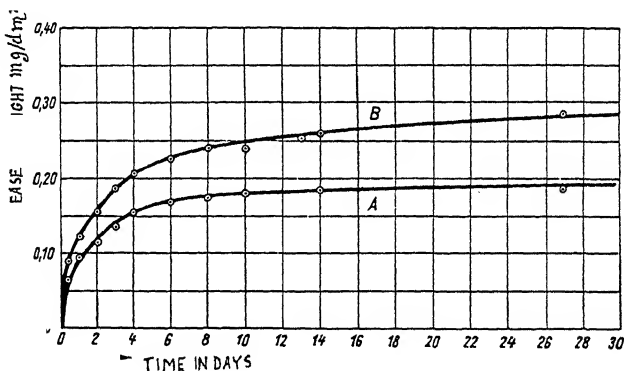
FIG. 13.—Oxidation of Aluminium in Air at Room Temperature; Increase in Weight with Time.

$A = 99 \cdot 98$ per cent. Al; $B = 99 \cdot 6$ per cent. Al.

this affinity is attributable the fact that aluminium on exposure to air becomes covered with a thin oxide film which protects the electropositive metal from further attack by atmospheric oxygen, and which is in fact responsible for that resistance to which the metal owes its multifarious applications as a structural material. Aluminium, in fact, exists under ordinary conditions in a passive state. The presence of impurities in the surface interferes with the uniformity of the film and lowers the resistance to corrosion.

W. H. J. Vernon has observed quantitatively the oxidation of aluminium in air at room temperature. He has shown by direct weighing the progressive increase in weight with time of test-pieces of 99·6 per cent. and 99·5 per cent. aluminium which have previously been carefully freed from their normal oxide coating. Fig. 13 shows

the increase in weight in mg. per dm². of surface in relation to time. The widely made assumption that a freshly prepared aluminium surface on exposure to air immediately becomes covered with an oxide film which opposes further access of oxygen is shown by these curves to be without foundation. The test-pieces were observed for a period of 27 days. The curves, initially steep, afterwards rise more gradually, and finally run approximately parallel with the horizontal axis. The flattening out of the curves shows that the absorption of oxygen by the aluminium is completed after some 14 days, which means that the oxide film attains its full protective effect only after this period.

By extending the tests to a period of 91 days the curious fact was observed that the weight continued to increase, although to a considerably less extent than initially. This additional weight increase took place at irregular intervals of time, actually occurring altogether three times during the test period of three months.
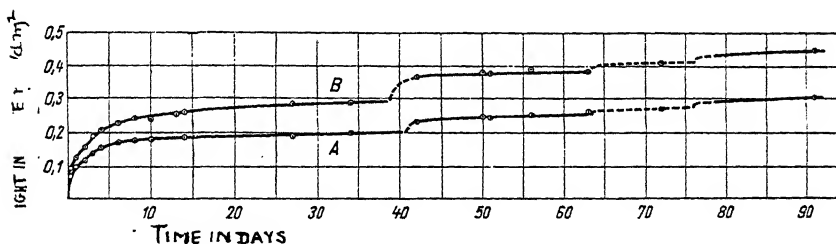
FIG. 14.—Oxidation of Aluminium in Air at Room Temperature. Increase in weight during prolonged oxidation; continuation of curves from Fig. 13. The dotted portions of the curves are hypothetical.

Vernon explained this phenomenon by assuming that the film developed cracks after it had reached the first complete growth stage, through which cracks oxygen gained further access to the metal, allowing oxidation to recommence, although in much diminished amount.

From the increases in weight observed during the first 27 days, and on the assumption that the film consisted of Al_2O_3 or the hydrated oxide $Al_2O_3 . 2H_2O$, Vernon calculated the thickness of the natural oxide film on the basis of the specific gravity. In both cases he arrived at a thickness of the order of magnitude of $1 . 10^{-6}$ cm. $= 0.01 \ \mu$.

Vernon's researches do not allow any definite conclusions to be drawn regarding the influence of the degree of purity of the aluminium on the course of oxidation at room temperature. Although the first researches had shown that the purer metal underwent oxidation more slowly and gave rise to thinner films, the later investigations, which were carried out with equal care, gave discordant results.

4

Pilling and Bedworth[1] observed the increase in weight of aluminium in air at 600° C. for 60 to 80 hours. No appreciable increase occurred after this time. They calculated the thickness of the resulting film as 0·0002 mm. = 0·2 μ, assuming the specific gravity to be normal.

Behaviour of Aluminium towards Aqueous Solutions

The behaviour of aluminium towards electrolytes is, in the same way as with other metals, to a large extent dependent on the purity of the metal. The presence of small traces of more electronegative constituents, which give rise to the formation of local elements, notably diminishes the resistance of aluminium. Since the investigations which have up to the present been made regarding the behaviour of aluminium have been carried out with few exceptions with commercial metal, the results which are discussed in the following do not apply to super-purity refined aluminium, which, as we shall see later, differs remarkably in its behaviour from the metal containing only a few tenths per cent. of impurities.

Action of Acids

In its behaviour towards acids, aluminium differs greatly from other metals. As we have seen, the dissolution of metals in acids consists in the replacement of the hydrogen ions of the acid by neutral metal atoms in accordance with the equation :

$$Me + H\cdot = Me\cdot + H.$$

On the basis of this hypothesis, the solution velocity depends solely on the hydrogen-ion concentration. Aluminium presents an exception, for its solution velocity is to a large extent dependent on the nature of the anions, as shown by its behaviour towards different acids : hydrofluoric acid and hydrochloric acid rapidly dissolve it, whilst hydrobromic acid and sulphuric acid dissolve it only very slowly, and according to M. Centnerszwer solution does not proceed to a measurable extent at all in normal nitric acid and in hydriodic acid.

The rate of attack by acids is determined by measuring the number of cubic centimetres of hydrogen evolved in unit time (one minute) per unit surface (1 cm.²) at 20° C. M. Centnerszwer has made an extensive study of this subject, and some of the results obtained are reproduced in Table VIII.

This table shows that the acids containing anions rich in oxygen scarcely attack aluminium, whilst the attack of the halogen acids

increases as the atomic weight of the halogen decreases, that is to say, from iodine to fluorine. M. Centnerszwer and W. Zablocki show, moreover, that the solution velocity in hydrochloric acid increases in the concentration range from 0·5N. to 4N., although the equivalent conductivity, and hence the dissociated portion of the acid, show decreases. From this fact they conclude that the reaction does not proceed between the aluminium and hydrogen ions, but between the metal and the undissociated molecules of the hydrochloric acid—in other words, that a typical substitution reaction takes place. This is in agreement with A. Hantsch's view, based on researches on the inversion of sugar, that the halogen acids must be considered as " pseudo-acids," in which it is the non-ionized portions, and not the hydrogen ions, which are responsible for the acidity.

If the results shown in Table VIII for normal solutions of strongly dissociated acids (HNO_3, H_2SO_4, HCl, HF) are compared, it can be

TABLE VIII

Atomic Weights of Halogens (approx.).	Acid.	Concentration of Acid.	Hydrogen evolved, cc./min./cm.^{2}
...	HNO_3	normal	almost 0
...	H_2SO_4	normal	almost 0
127	HI	normal	almost 0
80	HBr	normal	0·002
35·5	HCl	normal	0·233
19	HF	normal	0·383

seen that the ability to dissolve is to a large extent dependent on the nature of the anion. It is not the degree of dissociation of an acid, but the affinity of the aluminium for the anion which is the determining factor in the solution process.

E. Maas and W. Wiederholt arrived at a similar result on the basis of their researches. They showed that neither the total quantity of titratable acid nor the concentration of the free H· ions controls the extent of the attack, but it depends on the nature of the anion.

When aluminium undergoes solution in acids the solution velocity is initially small. It then rises slowly to a constant value which depends on the previous treatment of the metal, and the temperature and concentration of the acid. Palmaer has provided an explanation for this induction period, which he attributes to an initial increase in the number of local elements brought about by contact with the acid.

Of prime interest to our subject is the fact that hydrochloric acid and hydrofluoric acid differ greatly in their behaviour towards commercial aluminium from the acids with oxygen-containing anions.

In chromic acid solutions the solubility of the aluminium increases as the acid becomes more concentrated and as the temperature rises (*cf.* Table XII, p. 58).

Of the monobasic organic acids, formic acid exerts the strongest solvent action. Acetic acid attacks the metal more strongly in dilute solutions than in higher concentrations. The same applies to lactic acid. In dibasic acids solution proceeds appreciably more slowly. Oxalic acid attacks aluminium only slowly in cold solutions, but in hot solutions the attack is much more marked, and the metal is dissolved. The solvent action of succinic acid is extremely small, both in cold and in hot solutions.

Action of Bases

All alkaline solutions have a more or less solvent effect on commercial aluminium, the caustic alkalies, such as sodium and potassium hydroxides, having the strongest effect and dissolving the metal with liberation of hydrogen and formation of aluminates. The aluminium hydroxide, because of its amphoteric nature, behaves as if it were an acid towards these alkalies. Calcium hydroxide solution also attacks aluminium strongly; aqueous ammonia solutions exert a weaker solvent action.

According to K. Jabloczynski and E. Hermanowicz, the solution velocity of aluminium in sodium hydroxide is proportional to the square root of the concentration of the alkali. This has been confirmed by M. Centnerszwer and W. Wittand, and is valid also for very dilute solutions. A brief induction period, occupying only a few seconds, is observed when aluminium undergoes solution in sodium hydroxide similar to that observed with acids.

Action of Salt Solutions on Aluminium

In general, the heterogeneous impurities in virgin aluminium are more electronegative than the aluminium, so that they increase the extent to which the metal is attacked as a result of local element formation. The principal impurities present in commercial aluminium are iron and silicon, which are invariably present together, in quantities ranging from 0·2 to 0·5 per cent., according to the purity of the metal.

The iron is present as the compound Al_3Fe. The silicon may, according to J. Dornauf, either go into solid solution or be present as a heterogeneous constituent. As a consequence of the small potential difference between aluminium and silicon the influence of this element on the corrosion-resistance is not great. There is still a difference of opinion regarding the effect on the corrosion-resistance of aluminium of the iron to silicon ratio.

As with other metals, the general truth holds good that the corrosion-resistance increases with the degree of purity. Accurately described, commercial aluminium must be considered as a ternary alloy of the aluminium-iron-silicon system.

Among the salts, the chlorides, which are the principal constituents of sea-water, are of very great interest. They attack commercial aluminium. This attack may, depending on the purity of the metal, be brought rapidly to a standstill in air by the formation of a covering film of difficultly soluble aluminium compounds ; or it may take the form of local pitting, the pits once formed accelerating the attack and giving rise to actual perforation.

Reference must also be made to the salts of mercury, which attack aluminium with extreme rapidity, as does also metallic mercury. The mercury salt solutions have an " activating " effect, since they penetrate the natural oxide skin and react with the metal. The reaction proceeds as follows : the electronegative mercury is initially precipitated in metallic form on the aluminium, with which it combines to give an amalgam. The resulting local element is extremely active because of the big potential difference between the two metals. The aluminium, which behaves as the anode, is rapidly disintegrated to form oxide, which is visible as a white excrescence. Great care should be taken not to allow aluminium to come into contact with mercury or mercury salts.

In the following[1] will be found a summary of the behaviour of other salts.

Corrosion-reducing Additions (Stabilizers, Inhibitors)

Certain protective substances, which are called *stabilizers* or *inhibitors*, possess the ability, when added to the attacking medium in small quantity, of exerting a corrosion-reducing or immunizing influence. These substances are of great practical importance, and in many cases can completely inhibit attack. Reference may be made to the known measures for preventing attack by boiler feed water or to the use of economizers in the pickling of metals.

The addition of protective media may have three objects :

(1) A purely chemical action, in which the corroding substance is neutralized or removed by precipitation.

(2) An electrochemical action, in which the added substance shifts the potential of the local element in a direction favourable to the formation of protective films.

(3) The deposition of a colloid, which inhibits attack, on the metal surface.

[1] Pp. 55-65.

Some examples will be given of these different possibilities.

(1) Chlorinated hydrocarbons, such as trichlorethylene and carbon tetrachloride, are frequently used for the degreasing of metal surfaces. If the liquids are completely anhydrous there is no risk of the aluminium being attacked. When the liquids are allowed to stand for a length of time in air, however, they take up moisture which results in the formation of hydrochloric acid, which attacks the metal. In order to prevent this a small quantity of an organic base, such as triethylamine, is added to the chlorinated hydrocarbon in the first place, to neutralize any hydrochloric acid as soon as it is formed.

(2) Aluminium is dissolved by soda solution, with liberation of hydrogen. If potassium dichromate is added, the attack is inhibited. The potassium dichromate behaves as a strong oxidizing agent, exerting a depolarizing effect on the cathode of the local element by initially lowering the overvoltage of the hydrogen and assisting hydrogen discharge. The dichromate is simultaneously reduced by the hydrogen and precipitated on the metal in the form of a lower-valency chromium compound, and this layer acts as a basis for the formation of a protective film, which opposes further attack.

(3) The attack of soda solution on aluminium may also be prevented by the addition of water-glass. The inhibiting effect of this addition is explained by the deposition of a protective film of silicic acid gel on the anode of the local element, which offers a considerable resistance to the further passage of the current. An addition of organic colloids has a similar, though less effective, preventive action, as may be seen from Table IX. This table also gives corresponding values for caustic soda solutions. It shows that water-glass increases the attack by caustic soda, whilst the organic colloids prove comparatively good stabilizers. The figures given relate to hard-rolled 99·5 per cent. aluminium.

TABLE IX (according to H. Bohner and H. Röhrig)

Nature of Colloid (0·75 g. per 100 cc.).	10 per cent. Solution of Anhydrous Na_2CO_3. Reaction Period 30 mins.		10 per cent. Solution of NaOH. Reaction Period 30 mins.	
	Temp: 25°C. Loss in Weight, g./m²	Percentage Decrease of Attack.	Temp: 25°C. Loss in Weight, g./m²	Percentage Decrease of Attack.
Solution without colloid	9·68	...	31·07	...
,, with vegetable glue	8·34	13·86	10·58	66·0
,, ,, bone glue	4·53	53·25	15·99	48·5
,, ,, fish glue	3·57	63·20	10·97	64·7
,, ,, gum arabic	5·33	44·90	5·85	81·2
,, ,, agar-agar	5·06	47·70	5·13	83·6
,, ,, gelatin	5·31	45·20	17·88	42·3
,, ,, starch	8·06	16·75	11·25	63·8
,, ,, water-glass	0·00	100·00	35·23	−13·4

In the following some corrosive media with appropriate stabilizers are indicated :

Attacking Medium (or Solution)	Stabilizer
Potassium phosphate, 35 per cent., above 50° C.	Potassium dichromate.
Sodium carbonate (soda)	Water-glass, chromates, organic colloids.
Caustic soda	Chromates, organic colloids (*not* water-glass).
Caustic soda, 2 per cent.	0·1 per cent. hydrogen peroxide.
Higher fatty acids { Oleic acid, Palmatic acid, Stearic acid } at b.p.	Small addition of water.
Chlorinated hydrocarbons { Carbon tetrachloride, Trichlorethylene }	Organic bases (triethylamine, etc.).
Hydrogen peroxide	Water-glass.

Action of Different Substances on Commercially Pure Aluminium

Comprehensive investigations have been made by H. Bohner, H. Buschlinger and H. Röhrig to determine the behaviour of commercial aluminium towards a large range of substances. From the large number of compounds tested by these workers we have selected those which are of interest in connection with our considerations, and these are set out in the following pages (pp. 55 to 65). Unless otherwise stated the statements made refer to commercial 99·3 per cent. purity aluminium. In only a few cases is reference made to the difference which is frequently noted between the behaviour of hard-rolled and soft-annealed aluminium. It can be taken that, according to the nature of the attacking medium, either the hard or the soft material will have the greater resistance, but there is no general rule regarding which of the grades will behave the better. In the case of a great many substances there is virtually no difference between the chemical behaviour of hard-rolled and soft-rolled aluminium.

In all cases the nature and amount of impurities present in the surface of the metal, and their potential, compared with that of aluminium, determine the degree of attack.

Summary of the Chemical Attack of Different Substances on Commercial Aluminium

(Unless otherwise stated the solids are in aqueous solution)

Acetic acid.—Action only slight in cold solutions ; increases in hot solutions according to the concentration.

TABLE X

Loss in Weight in 24 hours, mg./dm.^{2}								
At room temperature :								
Acid concentration, per cent.	99·2	90	85	50	25	1	0·02	0·004
Loss in weight, mg./dm.^{2}	0·00	0·26	0·57	0·56	0·65	1·10	3·2	1·00
At boiling-point :								
Acid concentration, per cent.	99·9	90	70	40	5	1	0·2	
Loss in weight, mg./dm.^{2}	7	165	330	492	610	1200	770	

Aerated water (CO_2).—Practically no action.

Air.—Oxide skin forms at room temperature, and this affords protection against further attack (*cf. oxygen*).

Alcohol.—See *ethyl alcohol, methyl alcohol.*

Alkali metal chlorides, molten.—Remove oxide skin from aluminium ; used as fluxes in the melting, welding and soldering of aluminium.

Alum.—Slight attack which increases in hot solutions.

Aluminium chloride.—Rather strong attack.

Aluminium sulphate.—The attack may be rather strong or practically nil according to the content of free acid. Strongly basic aluminium sulphate, even in hot solution, has no action.

Ammonia.—Dry gaseous ammonia has no action.

Aqueous solutions containing less than 1 per cent. attack the aluminium initially, but the loss in weight is balanced by oxide formation, even in hot solutions.

Aqueous solutions containing more than 5 per cent. have a strong solvent action when hot.

Concentrated aqueous solutions (about 25 per cent.) attack aluminium initially, but the loss in weight is balanced by progressive oxide formation as time goes on (*cf.* Table XI).

TABLE XI

Reaction Period.	Loss in Weight, g. per m.	
	99·5 per cent. Al, hard.	99·5 per cent. Al, soft.
8 hours	20·5	17·2
16 ,,	10·7	10·0
24 ,,	9·6	4·9
32 ,,	7·2	2·9
8 days	6·9	1·5
14 ,,	6·4	−0·4 increase

Ammonium carbonate.—Practically no action.

Ammonium chloride.—In general the attack at room temperature is slight, but the action is stronger in hot solutions.

Ammonium nitrate.—Solid or molten : practically no attack. Aqueous solutions : practically no action.

Ammonium phosphate (diammonium phosphate).—Attack increases as the concentration increases and as the temperature rises.

Ammonium sulphate.—Slight attack.

Ammonium sulphide.—No action even in hot solutions.

Barium chloride.—Attack considerable, even at room temperature.

Barium hydroxide.—Attack initially rather strong, later inhibited by the surface film which forms.

Benzene.—No attack, even at boiling-point.

Borax.—Practically no action.

Boric acid, solution.—Practically no action at room temperature ; slight attack at boiling-point.

Bromine, liquid.—Strong attack once the natural oxide film on the aluminium has been penetrated. Attack by bromine water can be prevented by the addition of water-glass.

Butyric acid.—Attack rather strong to strong ; behaves similarly to acetic acid, *q.v.*

Calcium chloride.—Slight action which reaches a standstill (after 5 days) due to formation of a protective oxide film. After prolonged immersion (25 days) the oxide film dissolves and loss in weight is observed. The attack proceeds more readily in hot solutions.

Calcium hydroxide.—Strong attack.

Calcium sulphate.—Slight action.

Calcium sulphide.—Slight action.

Carbon dioxide, dry.—Practically no action at ordinary temperature.

Carbon disulphide.—No attack at ordinary temperature.

Carbon monoxide.—Practically no action at ordinary temperature.

Carbon tetrachloride.—When dry practically no action. In the presence of moisture, and particularly at high temperatures, some attack occurs (*cf.* pp. 54, 55).

Carbonic acid, dilute.—Practically no action.

Caustic potash.—See *potassium hydroxide.*

Caustic soda.—See *sodium hydroxide.*

Chile saltpetre.—See *sodium nitrate.*

Chlorinated hydrocarbons.—See *carbon tetrachloride, trichlorethylene.*

Chlorine, dry, gaseous.—No action at room temperature; strong attack at about 250° C., with formation of $AlCl_3$.

Chlorine water.—Vigorous attack (dissolution); the attack is diminished by the addition of water-glass.

Chromic acid.—Strong attack (solution) increasing with concentration and rise in temperature.

TABLE XII

Concentration of Acid.	Temperature, °C.	Loss in Weight after 150 hours, g./m.^{2}
1 per cent.	20	2·2– 2·75
5 ,, ,,	20	8·4– 9·7
10 ,, ,,	20	13·1– 13·25
Concentrated	20	43·2– 43·6
1 per cent.	60–70	2·2– 3·6
5 ,, ,,	60–70	12·9– 14·3
10 ,, ,,	60–70	26·3– 29·2
Concentrated	60–70	155·9–172·8

Citric acid.—Slight attack when cold; increased loss of weight when hot (see Table XIII).

TABLE XIII

Citric Acid Solutions and 99·4 per cent. Aluminium.
Test period 14 days

Temperature, °C.	Loss in Weight in Solutions of			
	1 per cent., g./m.^{2}	5 per cent., g./m.^{2}	10 per cent., g./m.^{2}	70 per cent., g./m.^{2}
20	0·3	0·3	0·3	0·3
60	—	11–11·5	—	—

Copper salts.—Strong attack (copper deposited on aluminium).

Diammonium phosphate.—See *ammonium phosphate.*

Distilled water.—See *water, distilled.*

Epsom salts.—See *magnesium sulphate.*

Ether.—No attack observed after 10 hours' contact with 99 per cent. aluminium at 35° C.

	Loss in Weight in g./m.² surface.	
	After 6 months.	After 12 months.
Aluminium, hard	0·24	0·24
Aluminium, soft	0·32	0·32

Ethyl alcohol.—Crude spirit : causes pitting.

96 per cent. alcohol : practically no action either at room temperature or when hot.

Absolute alcohol : practically no action either at room temperature or when hot.

Dilute alcohol : slight attack.

Fatty acids.—Lower : see *formic acid, acetic acid, butyric acid, propionic acid.*

Higher : see *oleic acid, palmitic acid, stearic acid.*

Ferric chloride.—Strong attack.

Ferrous sulphate.—Slight attack at 20° C.

Formic acid.—Attack rather strong in cold, and very strong in hot solutions.

Glycerin, pure (pharmaceutical quality).—Practically no action.

Hydriodic acid.—Scarcely any action.

Hydrobromic acid.—Strong attack, though considerably less than with hydrochloric acid.

Hydrochloric acid.—Rapidly dissolves commercial Al both in cold and hot solutions. Refined Al (99·98 per cent.) produced by the Hoopes process is only slightly, or not at all, attacked by dilute hydrochloric acid.

Hydrofluoric acid.—Strong attack at all concentrations and temperatures. The action is uniform and hydrofluoric acid is, therefore, used as an etchant.

Hydrogen peroxide.—Action may be negligible or rather strong depending on concentration and temperature. Soft-annealed Al is less attacked than hard-rolled metal (see Tables XIV and XV, *cf.* also p. 55 (*Stabilizer*)). Attack by H_2O_2 is largely dependent on the nature of the substance added to it, which may either increase or decrease the attack. Addition of water-glass inhibits corrosion, whilst HCl accelerates attack.

TABLE XIV

1 per cent. Hydrogen Peroxide Solution.					
Al.	Temperature, °C.	Loss in Weight		Variation in Tensile Strength.	Decrease of Elongation.
		After 10 days.	After 26 days.		
99·2 and 99·5 per cent.	20 60 60–70	insignificant ,, slight attack without loss in weight	insignificant ,, slight attack without loss in weight	nil ,, ,,	slight ,, 10–20 per cent.

TABLE XV

Hydrogen Peroxide.		
Al.	Loss in Weight after 10 days, g./m.²	
	3 per cent. Solution.	30 per cent. Solution.
99·5 per cent., hard-rolled . .	2·5	15·8
99·5 per cent., soft-annealed . .	nil	2·1

Hydrogen sulphide.—Practically no action.

Iodine.—Dry, solid : no action at ordinary temperature.

Aqueous solutions : also no action.

Tincture of iodine (alcoholic solution) : attack rather strong with evolution of heat.

Iron chloride.—See *ferric chloride.*

Lactic acid.—Up to 10 per cent. practically no attack at 20°C. ; in hot solution attack appreciably increases ; behaves similarly to acetic acid.

Magnesium chloride.—Low concentrations (under 1 per cent.) cause pitting. Higher concentrations produce uniform coating and no further attack.

Magnesium sulphate.—Practically no action even in hot solution.

Mercury.—Strong attack in the presence of atmospheric moisture, during which the Al is disintegrated with the formation of alumina ; further corrosion by mercury may be prevented by treating the surface with 10 per cent. potassium dichromate solution. Absolutely dry mercury in dry air does not attack Al so long as the natural oxide skin is not injured (*cf.* p. 53).

Mercury salts.—Strong activation with formation of amalgam and disintegration due to oxidation (*cf.* p. 53).

Methyl alcohol.—Slight attack.

Milk of lime.—See *calcium hydroxide.*

Nitric acid.—In general attack very slight. According to M. Bosshard the strongest attack on 99·3 per cent. Al occurs with 30 per cent. acid (*cf.* Figs. 15 and 16). As the temperature increases the attack by nitric acid becomes considerably stronger. A rise in temperature from 20° to 60°-70° C. accelerates the solution velocity about tenfold. The action of acid in movement is smaller than that of still solutions.
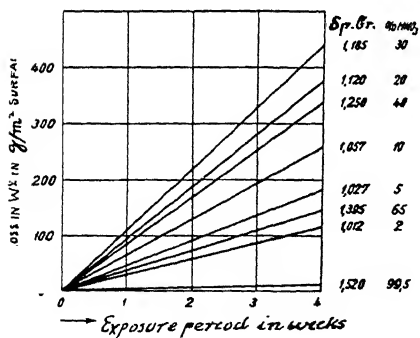

FIG. 15.—Progress of Dissolution of Hard-rolled 99·3 per cent. Aluminium in Nitric Acid of Different Concentrations at 20° C.
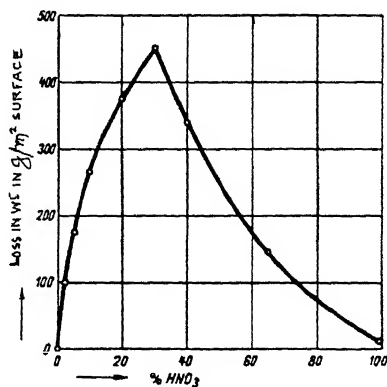
FIG. 16.—Loss in Weight of Hard-rolled 99·3 per cent. Aluminium in relation to the Nitric Acid Concentration after a Test Period of 4 weeks.

Oleic acid.—If water is completely absent oleic acid has practically no action, even when hot. Local corrosion is produced by boiling acid. Traces of water completely prevent attack.

Oxalic acid.—Slight attack in cold solutions of any concentration; strong attack (dissolution) by hot solutions.

<div align="center">TABLE XVI</div>

Loss in Weight of 99·4 per cent. Aluminium in 14 days, mg./dm.²					
Acid concentration, per cent. .	0·4	0·5	2·0	5·0	10·0
At room temperature $\left\{\begin{array}{l}\text{hard Al}\\ \text{soft Al}\end{array}\right.$	59·4 58·8	52·2 60·0	122·4 121·2	120·6 114·6	116·4 139·8
At 70° to 80° C. . $\left\{\begin{array}{l}\text{hard Al}\\ \text{soft Al}\end{array}\right.$	— —	75·0 72·0	428·4 474·0	1146·0 1086·0	1555·2 1309·8

Oxygen.—An oxide skin forms at ordinary temperature and after reaching a certain thickness protects the metal from further oxidation. As the temperature rises the thickness of the oxide skin increases (*cf.* Vernon, pp. 48-49; Pilling and Bedworth, p. 50). Al when raised to a red heat burns in oxygen with a brilliant flame and the evolution of much heat.

Palmitic acid.—Behaves similarly to stearic and oleic acids, *q.v.*

Paraffin.—Practically no action.

Petroleum ether.—No attack at room temperature ; negligible attack when hot.

Phosphoric acid.—Attack increases (dissolution) with increasing concentration and rise of temperature ; attack decreases with increasing purity of the Al. H. Röhrig and K. Geier state that the addition of sodium carbonate considerably diminishes the attack.

Potash alum.—Slight attack at 20° C.; action greater in hot solution.

Potassium bromide.—Slight attack at 20° C.; rather strong attack at boiling-point.

Potassium carbonate.—Strong attack, which may be reduced by addition of water-glass or a chromate.

Potassium chlorate.—No action, even at boiling-point.

Potassium chloride.—Slight to rather strong attack; similar to sodium chloride.

Potassium chromate.—Practically no action even at boiling-point.

Potassium cyanide.—Rather strong attack at 20° C.; strong attack at boiling-point.

Potassium dichromate.—Practically no action, even at boiling-point; protective oxide film formed.

Potassium hydroxide.—Strong attack, which may be reduced by addition of hydrogen peroxide or a chromate.

Potassium nitrate.—Practically no action, even in hot solution.

Potassium nitrite.—Practically no action, even in hot solution.

Potassium permanganate.—No action in cold solution; slow attack in boiling solution.

Potassium silicate.—See *water-glass.*

Propionic acid.—Behaves similarly to acetic acid, *q.v.*

Pyrogallic acid.—No action, even at boiling-point.

Sea-water.—Moderately strong attack, which diminishes with increase in purity of Al.

Soda.—See *sodium carbonate.*

Sodium bicarbonate.—Slight attack.

Sodium borate.—See *borax.*

Sodium carbonate (soda).—Rather strong attack, which may be prevented or diminished by addition of water-glass or a chromate.

Sodium chlorate, free from chloride.—Practically no action.

Sodium chloride (common salt).—Slight to strong attack, which, depending on the purity of the aluminium, sooner or later comes to a standstill as a result of the formation of a protective oxide film; a rise in temperature increases the attack.

Sodium hydroxide.—Strong attack (dissolution); for concentrations below 0·5 g. per litre attack negligible. Addition of water-glass increases attack, but a chromate or hydrogen peroxide diminishes attack.

Sodium nitrate.—Practically no action, even in hot solution.

Sodium nitrite.—Practically no action.

Sodium phosphate, Na_3PO_4.—Rather strong to strong attack.

Sodium silicate.—See *water-glass*.

Sodium silicofluoride.—Up to 1 per cent. slight etching with formation of black protective film.

Sodium sulphate.—Very slight action, even in hot solution.

Sodium sulphide.—Strong attack when hot (40° to 50° C.).

Sodium thiosulphate.—Practically no action.

Steam.—See *water*.

Stearic acid.—No action, even when hot, if completely anhydrous. Some attack at boiling-point, which is completely prevented by small traces of water.

Succinic acid.—No detectable attack by 1 to 50 per cent. acid at 100° C. after 10 hours.

Sulphur.—Molten sulphur or sulphur dissolved in carbon disulphide has no action.

Sulphur dioxide.—Gaseous : practically no action, by neither the dry nor the moist gas, even when hot.

Liquefied : when anhydrous no action, even when hot.

Aqueous (sulphurous acid) : rather strong to strong attack (dissolution) according to the concentration of the acid. The loss in weight of 99·4 per cent. Al after 10 days is as follows :

Concentration of Solution, per cent.	Loss in Weight, g./m.²
0·2	3·0– 4·5
3·0	6·3– 7·4
5·0	9·9–10·7
10·0	11·8–12·0

Sulphuretted hydrogen.—See *hydrogen sulphide*.

Sulphuric acid.—Very slight to strong attack (dissolution) depending on the concentration ; attack increases as temperature rises.

Sulphurous acid.—See *sulphur dioxide.*

Tannin.—Practically no action.

Tartaric acid.—Slight attack when cold ; increased attack when hot.

Trichlorethylene.—When anhydrous, no action, even at boiling-point. If a few drops of water are added loss of weight occurs (*cf.* p. 54).

Water.—Distilled : action practically nil or negligible ; reaches standstill after formation of a protective oxide film. Formation of oxide accelerated in hot distilled water.

> Rain-water : slight to strong attack.
>
> Condenser water : slight to strong attack.
>
> Tap-water : slight to strong attack according to the nature of the water.
>
> Sea-water : slight to strong attack according to purity of Al.
>
> Steam : dry steam has practically no action ; saturated steam gives rise to loss in weight ; *cf. carbonic acid.*

Water-glass.—Soda water-glass : practically no action.

> Potassium water-glass : slight attack (etching) in certain cases.

Chemical Behaviour of Super-purity Aluminium

M. Centnerszwer[1] investigated the behaviour of 99·95 per cent. aluminium towards hydrochloric acid and alkaline solutions. In dilute hydrochloric acid this metal dissolves about fifty times more slowly than 99 per cent. aluminium. The region of acid concentration in which super-purity aluminium is attacked is shifted appreciably higher. Measurable dissolution at 25° C. occurs only above a concentration higher than 2N.

In caustic soda super-purity aluminium exhibits the same behaviour and the same solution velocity as 99 per cent. aluminium. Super-purity aluminium also dissolves in dilute ammonia with a measurable velocity. According to Centnerszwer the dependence of the solution velocity of the aluminium on the square root of the hydroxyl ion concentration signifies that on dissolution in alkaline solutions the dissociation products of the hydroxyl ions, *i.e.* probably oxygen ions, according to the equation $OH' \rightleftarrows O'' + H\cdot$, take part in the reaction (*cf.* p. 12).

[1] *Cf.* p. 50.

According to R. Gadeau[1] the super-purity aluminium of 99·99 per cent. content exhibits a conspicuous resistance to acids.   Fig. 17 shows the loss in weight per dm.[2] of surface of aluminium of different degrees of purity (99·5, 99·90, 99·95 and 99·99 per cent.) in hydrochloric acid solutions of different concentrations.   The test-pieces, $100 \times 100 \times 1$ mm. in size, were etched in sodium carbonate solution before commencing the tests.   The test-pieces of 99·5 per cent. aluminium were completely disintegrated at the end of half an hour in hydrochloric acid of 23° and 82·5° Bé.   In hydrochloric
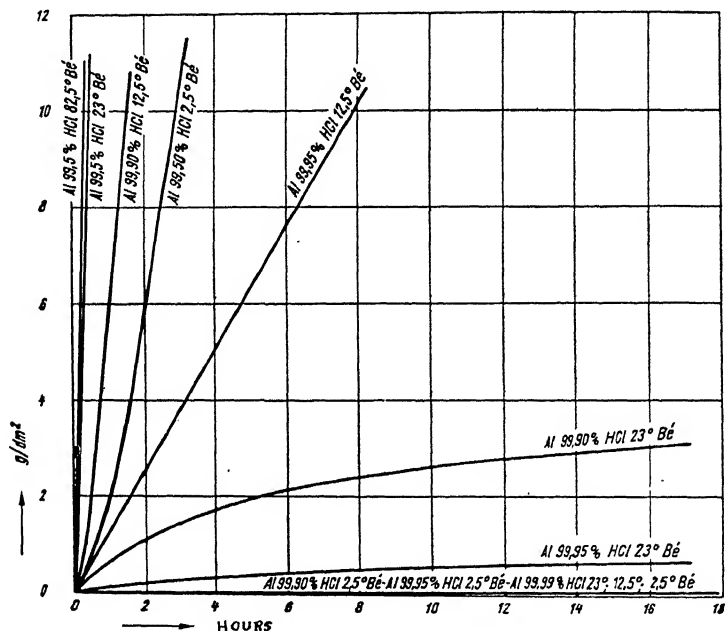

FIG. 17.—Loss in Weight with Time of 99·99 and 99·5 per cent. Aluminium in Hydrochloric Acid Solutions of Different Concentrations.

acid of 2·5° Bé. the loss in weight was 11 g./dm.[2] after three hours. In contrast to this the 99·99 per cent. Al in concentrated hydrochloric acid lost only 0·06 g./dm.[2] after 16 hours, and 0·044 g./dm.[2] in hydrochloric acid of 2·5° Bé. after 52 hours.

Behaviour of Aluminium Alloys

The German Standard Specification DIN 1713[2] provides a summary of the commercially important aluminium alloys.   From the eight groups of forging alloys and eight groups of casting alloys categorized in this Specification we can differentiate five main

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[1] Cf. p. 6.   [2] Second Edition, Sept., 1937.

groups on the basis of the predominance of one constituent, and of the resulting behaviour towards salt solutions :

Group.	Principal Constituents other than Aluminium.	Forging Alloys.	Casting Alloys.
1. Copper-containing alloys	Cu (Mn, Si)	Lautal	American alloy, Neolanium (containing Mg.)
	Cu-Mg (Si, Mn)	Duralumin, Bondur, Ulminium, Silal, etc.	—
	Cu-Ni (Mg)	Duralumin W, Y-alloy	Y-alloy
2. Zinc-copper-containing alloys	Zn-Cu	—	German alloy
3. Magnesium-containing alloys	Mg (Mn)	Hydronalium, BS-sea-water, Duralumin, Peraluman 7, Hedronal	Hydronalium, BS-sea-water, Duralumin, Peraluman, Stalanium
	Mg-Si (Mn)	Aludur 533, Duralumin K, Legal, Anticorodal, Pantal, Ulmal, Polital (containing Ni)	Anticorodal, Polital, Pantal 5, Nural 43
	Mg-Mn (Sb or Ti)	KS-sea-water, Peraluman	KS-sea-water, Titan-sea-water, Cast Pantal, Peraluman, Duranalium
4. Silicon-containing alloys	Si (11–13·5 per cent.)	Silumin	Silumin
	Si-Mg (Mn)	—	Silumin-gamma
	Si-Cu	—	Copper-silumin
5. Manganese-containing alloys	Mn (1–2 per cent.)	Aluman (AW 15), Mangal, Heddal, Silal, Wicromal	—

In this table the principal alloying constituent is placed first. Where there are several important constituents the predominating constituent is placed first and is separated from the second important constituent by a hyphen. The constituents in brackets are those present in smaller quantity. In cases where there is only one constituent the percentage content is stated. The third and fourth columns give the names of some forging and casting alloys to serve as examples.

1. The copper-containing forging alloys of the first group with 3·5 to 6 per cent. copper content are heat-treatable and are used for highly stressed components. The corrosion-resistance of these alloys and of the casting alloys of the same group leaves much to be desired in their behaviour towards sea-water. In order to protect them from corrosive attack they are plated either with copper-free aluminium alloys or with 99·5 per cent. aluminium, or they are provided with a protective oxide film.

2. The aluminium casting alloy known as German alloy, with 8 to 12 per cent. zinc and 2 to 5 per cent. copper content, likewise requires corrosion protection, since it is readily attackable, due to the content of more electronegative metals.

3. The magnesium content bestows improved chemical resistance on the alloys of the third group. The aluminium-magnesium alloys, poor in silicon, with and without the addition of manganese or antimony, possess high resistance to sea-water. The manganese content gives rise to the formation of protective films containing manganese oxide. The antimony-containing aluminium alloys form antimony oxychloride surface films on exposure to chloride-containing solutions, and these films become converted by the action of oxygen to antimony oxide. Both compounds exert a good protective effect.

G. Siebel explains the resistance of the aluminium-magnesium alloys to sea-water on the basis that magnesium goes into solution as anode in the local element with the liberation of hydrogen and the formation of magnesium chloride and sodium hydroxide. The latter partly dissolves the aluminium, and the magnesium ions are precipitated as magnesium hydroxide. The magnesium, which is insoluble in caustic soda, becomes covered with an oxide or hydroxide film which prevents further attack. Siebel further shows that in the aluminium-magnesium alloys the properties of the magnesium, which is insoluble in alkalies, become evident as the magnesium content increases by rendering these alloys more resistant towards weak alkaline solutions and, conversely, less resistant towards the majority of weak acids than pure aluminium. This alkali-resistance of magnesium, and the small potential difference between aluminium and magnesium are, therefore, of great importance in determining the corrosion-resistance of the high-percentage aluminium-magnesium alloys towards sea-water and salt solutions. There is practically no difference in the corrosion behaviour of these alloys in the homogeneous condition produced by heat-treatment and in the heterogeneous condition. Nevertheless, any microscopic blow-holes produced during solidification of castings may give rise to local pitting. Formation of such blow-holes can be effectively countered by addition of silicon (up to 1 per cent.).

4. The silicon-containing aluminium alloys are known by the

name of Silumin, and are widely used because of their good casting properties. A fine grain can be produced in the castings by addition of sodium. The casting properties are improved by adding magnesium (Silumin-gamma). In spite of the very slight potential difference which exists between aluminium and silicon, the attackability of Silumin is greater than that of commercially pure aluminium. Where the alloys are to be exposed out-of-doors under stress, more particularly in sea air, it is necessary to provide a protective film.

5. The investigations carried out by W. Helling provide information regarding the resistance of aluminium-magnesium alloys towards chemical influences. Before these investigations were carried out it had been shown that a protective film containing manganese oxide was formed on the aluminium-manganese alloys on exposure to chemical attack. M. Bosshard had demonstrated that with additions of 0·5 to 1 per cent. of manganese the corrosion-resistance towards hydrochloric acid was lessened, but with further additions of manganese was appreciably improved. Helling investigated the influence of manganese contents ranging from 1 to 3 per cent., and of heat-treatment at 400° and 600° C., on the attack of caustic soda, sulphuric acid, aqueous sulphurous acid, flue-gases containing sulphurous acid, acetic acid, steam, sodium chloride solutions containing hydrogen peroxide, and an aqueous mixture of equal parts of nitric and hydrochloric acids.

The results are briefly summarized in the following :

Attacking Substance.	Behaviour of Al-Mn alloy with 1·2 to 3 per cent. Mn, with and without heat-treatment at 400° and 600° C.
NaOH, 0·5 per cent.	Corrosion-resistance increases with increase in Mn content.
NaOH, 0·5 per cent.	Attack independent of Mn content.
SO_2-containing flue-gases, 2 per cent. aqueous SO_2 solution, 2 per cent. H_2SO_4	Resistance decreases with increase in Mn content.
H_2O_2-containing NaCl solution (3 per cent. NaCl, 1 per cent. H_2O_2)	In general, resistance increases with increase in Mn content. The influence of the intermediate annealing temperature is different with different alloys.
Acetic acid, 40 per cent.	No definite connection between Mn content, heat-treatment and loss in weight.
Steam	Slight loss in weight ; no appreciable difference with different alloys.
Mixed acids, $HNO_3 : HCl : H_2O$ $= 4 : 4 : 1$	No definite influence of Mn content on the loss in weight, which is in some cases very large.

Helling summarizes the results of his investigations as follows : these investigations show that the widely held view that the corrosion-resistance of aluminium-manganese alloys is better than that of pure aluminium, is not generally true. No investigations were carried out by Helling on resistance towards atmospheric corrosion or sea-water, and the literature only contains a few generalizations on the subject.

S. Daniels investigated the behaviour of aluminium alloys with manganese contents of from 1 to 9·6 per cent. towards distilled water and towards 20 per cent. sodium chloride solutions, but his results cannot be considered reliable, since the test period was too short. The tests in distilled water were carried out for 30 days, but those in sea-water were only carried out for 100 hours. The corrosion in water of all the manganese alloys was less than that of an aluminium alloy containing 8 per cent. of copper, which was tested at the same time. The corrosion in salt water was less than that in distilled water at the end of 24 hours. No difference in behaviour between the alloys with different manganese contents was observed.

CHAPTER VI

ELECTROLYTIC BEHAVIOUR OF ALUMINIUM AND OTHER VALVE METALS

Historical Survey

IF direct current of sufficient voltage is applied to an electrolytic cell filled with dilute sulphuric acid, at room temperature, and provided with platinum and aluminium electrodes, the aluminium being made anode, the current, which is initially high, rapidly falls off, and reaches as time goes on a final value which is only equal to a small fraction of the initial current. H. Buff, who observed this peculiar behaviour of an aluminium anode as far back as 1857, attributed the bad current conduction to the dark silicon layer which formed on the aluminium, and which was due to the high silicon content of the metal available at that time. The degree of impurity of the material used by Buff is clear from the fact that silicon hydride was discovered by Wöhler and Buff in a joint research on the anodic behaviour of aluminium in sodium and ammonium chloride solutions carried out in the same year. The falling off of the current observed in sulphuric acid did not occur in the chloride solutions, nor in dilute hydrochloric acid : the barrier effect was absent. The analogy in the behaviour of anodically polarized aluminium and of aluminium not exposed to the action of an electric current towards sulphuric acid and hydrochloric acid merits special attention.[1]

E. Ducretet attributed the phenomena at the aluminium anode to the formation of an aluminium oxide film, a view which W. Beetz upheld in one of his later articles. Ducretet further demonstrated that in an arrangement similar to that used by Buff, the current flows unhindered through the cell as soon as the aluminium is made the cathode. In this case the galvanometer included in the circuit registered a deviation of 22 divisions, but when the direction of the current was reversed, that is to say, when the aluminium was made the anode, the deviation of the galvanometer needle was only 2 divisions. This considerable resistance towards the passage of the current is permanent. Ducretet was able to show a similar rectifying effect at an iron anode, but in this case the behaviour

[1] See p. 51 (Table VIII).

was irregular. This unipolar or unidirectional conduction in dilute sulphuric acid did not occur in the case of other metals, such as gold, silver, platinum, copper, zinc, magnesium, tin and lead. Ducretet recommended the use of the aluminium cell for circuits where only one direction of current is permissible. The aluminium cell in this case is thought of as an electric valve.

Beetz investigated quantitatively the increase in weight of an aluminium anode in sulphuric acid, and the amount of oxygen liberated as gas and contained in the dissolved aluminium sulphate, but he arrived at a quantity of oxygen which was far below that which would theoretically be expected from the current consumption. In a later article he was able to explain the reason for this. He had worked with too small a current density. The tiny oxygen bubbles which were produced in consequence were largely dissolved by the electrolyte and were, therefore, able to escape into the air outside the eudiometer. On using larger current densities the larger gas bubbles evolved were able to enter the eudiometer and were not absorbed by the progressively hotter electrolyte. In this case, owing to contamination with hydrogen, there was apparently even a small excess of oxygen. In order to avoid this, in other words, to prevent attack of the metal by the sulphuric acid, the electrolyte had to be cooled.

" From now on," writes K. Norden, " the phenomena will have to be relegated to a domain of pure physics which will explain the nature of unipolar conduction on the basis of the fundamental notions of electrical theory. F. Kohlrausch, by his basic investigations on the polarization capacity of metal electrodes, opened up the way to a new conception of the phenomena. In accordance with this conception the film deposited on the electrode behaves in the same way as the dielectric of a condenser, one of whose plates is formed by the metal and the other by the ions surrounding the electrode (not, as is often stated, by the liquid, since only the ions can carry electric charges)."

Starting from the general ideas regarding electrolytic condenser effects, A. Oberbeck investigated the galvanic polarization of different metals, which permitted a calculation of the capacity of polarized electrodes. The electrolyte which he selected for his investigations was concentrated sodium chloride solution, which is the least suitable for our considerations. We have already seen that the rectifying effect does not occur at an aluminium anode in this solution.[1] Nevertheless, it should be noted that Oberbeck recognized the exceptional position which aluminium occupies as compared with the other metals he investigated.

[1] p. 71.

F. Streintz discusses electrolytic polarization in several articles which yield interesting information regarding the behaviour of aluminium.

In one of these articles he describes the anodic behaviour of different metals and points out the abnormal behaviour of aluminium compared with other metals. The " oxygen polarization " increases in dilute sulphuric acid roughly proportionally to the applied voltage up to a value of 17 volts, and " probably still higher." A further distinguishing criterion of the anodic behaviour of aluminium is the rapid decline of this polarization after the circuit has been opened. These two phenomena, taken together with the fact that the aluminium oxide formed at the anode is " a rather poor electric conductor," give rise to the conjecture that they are caused by a condenser effect. The anode, converted into a condenser and charged by the polarizing current, should exhibit a short discharge current on earthing once the current source is disconnected. The needle of a galvanometer inserted in the earth connection does not, however, revert to its position of rest after the first current impulse, but very slowly swings back towards this position. Streintz conjectures that this is due to the galvanic polarization and that, therefore, the total polarization current supplied by an aluminium anode is made up of the sum of the dielectric or condenser polarization and the electrolytic polarization. He remarks, however, that the separation of these two quantities would be a difficult undertaking.

The first proposal for the practical application of the aluminium cell as a rectifier for alternating currents was made by Hutin and Leblanc in 1891. E. Haagn, using an aluminium cell as a condenser of variable capacity, obtained satisfactory results for the measurement of the internal resistance of galvanic cells by Nernst's condenser method. The arrangement was such that the aluminium electrodes could be more or less immersed in the dilute sulphuric acid by means of a positioning device. The forming of the aluminium cell was suitably carried out with a voltage in excess of that of the service current. Haagn recommended that the aluminium plates should be thoroughly rinsed after use and allowed to stand in air, or else be wholly immersed in the sulphuric acid. If they were only partially immersed in the liquid the plates were strongly corroded, a thick crust of aluminium sulphate being formed after quite a short time.

In an article on the phenomena of polarization at metallic membranes, A. M. Scott discusses the influence of the polarization produced by an external E.M.F. on the capacity of an aluminium cell. Whilst the behaviour of aluminium when made the cathode is not of special interest, an insulating film is formed on the aluminium anode, and this conditions the capacity of the cell. In other words, the cell behaves as a condenser.

In 1897 L. Graetz and Ch. Pollak published almost simultaneously, and quite independently, their researches on the electrolytic rectifier. L. Graetz used aluminium and carbon as the electrodes for his rectifying cell, and he employed dilute acid or alum solution as electrolyte. In the direction in which aluminium was the anode this cell allowed " no current measurable with a sensitive galvanometer " to pass[1] so long as the voltage was less than 22 v. In the opposite direction, however, the current was only slightly weakened. If an alternating current is sent through such a cell, and if the anodic polarization exceeds the voltage of the alternating current, or is at least equal to it, only the negative portion of the current can pass. This means that the portion of the current passing in a given direction is abstracted from the alternating current, giving an interrupted direct current through the circuit. In the arrangement which Graetz adopted, using four such cells, it is possible to convert alternating current completely into pulsating direct current. Pollak used a similar arrangement for his electrolytic rectifier, but he employed alkaline or neutral solutions of salts of phosphoric acid, of dibasic organic acids, or of hydroxy, aldehydic or ketonic acids. With these electrolytes it was possible to utilize the cell as a rectifier so long as it contained only one aluminium electrode. If two aluminium electrodes were employed he obtained a condenser. Both may be used up to voltages of 140, whilst the rectifier effect in the electrolytes proposed by L. Graetz failed at voltages as low as 22.

The oxide films formed in alkaline or neutral solutions on aluminium are extremely thin. Pollak attributed the large capacity of his condenser to this small film thickness, since the capacity could be further increased by enlarging the surface of the aluminium sheet. Graetz's explanation of the rectifying effect of the aluminium electrode approximates very closely to the view held by Streintz.[2] According to his conception, there occurs, in addition to the electrolytic polarization, a dielectric polarization and condenser effect due to the badly conducting oxide film, which is opposed as an E.M.F. to the applied voltage. Graetz estimated this opposing force[3] as 22 v.

In this connection an observation made by E. Wilson is worthy of notice. He showed that sulphuric acid and alum solution at elevated temperatures lose the property of imparting a high polarization to the aluminium anode when the current passes. C. Liebenow succeeded in overcoming this difficulty by using an ammonium bicarbonate solution for his electrolytic rectifiers and condensers. With this electrolyte the polarization falls off only to a very small extent at elevated temperatures, so that practically no interference is to be expected. In 1900 the Allgemeine
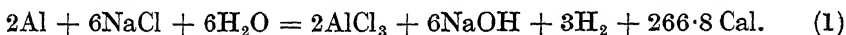
[1] *Cf.* E. Lecher, p. 78.   [2] See p. 73.   [3] *Cf.* E. Lecher, p. 78.

Elektricitätsgesellschaft took out a patent for the use of weakly acidified solutions of organic magnesium or aluminium salts for condensers and rectifiers.   Siemens & Halske A.-G. recommends the use of aqueous solutions of magnesium or calcium bicarbonate, of mandelates of the earth metals or alkaline earth metals, or of acidified solutions of organic ammonium salts for the same purpose.

In 1898 an article by A. Ditte was published which reviewed the chemical behaviour of aluminium.   Ditte first observes that aluminium owes its apparent chemical resistance only to the presence of the natural oxide film which invariably covers its surface.   Once this film is injured or removed, the attack of different chemicals— in fact of the majority of chemicals—on the metal becomes more or less energetic.   If accurate observation is undertaken it may, however, be shown that aluminium actually reacts instantaneously when in contact with dilute acids (with the exception of the halogen acids), but that the reaction comes to a standstill after a short time once the metal becomes covered with a gas film, which adheres strongly to it.   This hydrogen can be removed *in vacuo*, and then the aluminium can be gradually brought completely into solution. From this point Ditte discusses thoroughly the reaction of salt solutions, more particularly of chlorides, on aluminium.   The following reactions take place in a common salt solution :

$$2Al + 6NaCl + 6H_2O = 2AlCl_3 + 6NaOH + 3H_2 + 266\cdot8 \text{ Cal.} \quad (1)$$

$$2AlCl_3 + 6NaOH = Al_2O_3 + 6NaCl + 3H_2O + 177\cdot5 \text{ Cal.} \quad (2)$$

Basically, therefore, the reaction consists of the action of water on aluminium.   In spite of its positive heat tone it comes to a standstill, since the alumina film formed is not dissolved by the sodium chloride solution.   Owing to the separation on the one hand of alumina, and on the other of hydrogen, the aluminium remains apparently unchanged both in the salt solution and in acid, in spite of the fact that it should be energetically attacked by both, since it is oxidizable by pure water.   Conditions are quite otherwise, however, once the salt solution is combined with an acid, *e.g.* sodium chloride solution with acetic acid.   In this case, the acid continuously neutralizes the caustic soda formed in equation (1), so that the reaction represented by equation (2) can no longer occur.   In such a mixture the hydrogen adheres only loosely to the aluminium surface, so that it may be seen to evolve, whilst the metal goes into solution.   It is sufficient, therefore, to add a few drops of acetic acid to a salt solution, in which aluminium remains unchanged, to induce liberation of hydrogen, which continues until the acid is used up.   If the reaction is brought to a standstill, an addition of a further small quantity of acid will renew the hydrogen liberation.   The same applies to other acids, such as tartaric acid, oxalic acid, stearic acid, etc.   The bromides and iodides

of the alkali metals behave in the same way as the chlorides, and so also do the corresponding salts of the alkaline earth metals.

K. Norden[1] is of the opinion that the possibility of solving the problem of the aluminium anode depends on whether it is possible to determine with certainty the chemical nature of the coating which adheres rigidly to the aluminium. To do this, the film must first be separated from the metal. Since, however, mechanical separation cannot be carried out, because the film is too firmly anchored in the metal, K. Norden devised the method of cathodically polarizing for a long period at high current density aluminium which had been formed anodically in dilute sulphuric acid, and then making the aluminium the anode again, by which means it was possible to segregate a sufficient amount of the film. . By determining the quantity of gas which separated, he proved that no reduction of the aluminium oxide occurred due to the hydrogen produced during the period as cathode. The experimental arrangement is described more precisely by Norden than is the case in the previously mentioned articles by other research workers. He separated the anode and cathode regions, utilizing two beakers joined by a glass siphon tube. The ends of the siphon were surrounded by a parchment membrane. The electrolyte, which consisted of dilute sulphuric acid of sp. gr. 1·050, was maintained at a temperature of 20° to 30° C. by means of a lead cooling coil, which also cooled the siphon. The anode consisted of an aluminium wire 4 mm. in diameter, the purity of the metal being about 98·9 to 98·7 per cent. The anode surface was first cleaned with emery and dilute sulphuric acid. An accumulator of 115 v. was used for the current supply, the current being controlled by resistance lamps. Throughout the experiments quantitative observations were made of the amounts of aluminium, electrolyte and gases (hydrogen, oxygen). The most important of the results are given on the opposite page in the form of a table, for the sake of brevity.

Norden, on the basis of very roundabout arguments, deduces from his results that aluminium hydroxide, $Al(OH)_3$, is primarily formed at the anode. The solubility of this hydroxide is accepted by him as the explanation for the mechanism of current conduction,

"which must remain incomprehensible if the coating on the anode is insoluble. In such a case it would not be possible to understand in what manner the ions could neutralize their charges, *i.e.* conduct the current, unless fresh metallic surfaces, at which the ions could be discharged, were continually being exposed by chemical dissolution of the coatings."

Quite apart from the fact that the assumption of the primary formation of aluminium hydroxide has no experimental foundation,

the hypothesis made by K. Norden appears superfluous, in so far as, in the same article, he had already shown that the existing film is soluble in acids and alkalies.[1] It is, however, important that Norden in this way drew attention to the fundamental difference between electrolytes which have and those which have not a solvent effect on the film.   He concluded that in electrolytes in which the coating may be considered to be practically insoluble, *e.g.* in neutral salt

TABLE XVII

Test Results.	Remarks.
1. The cathodically polarized aluminium is not dissolved by the dilute sulphuric acid when the current passes.	The cathode becomes surrounded with a protective hydrogen envelope as the current passes.
2. About 4 per cent. of hydrogen in excess of that which would correspond to the theoretical value required by Faraday's law is evolved.	The excess of hydrogen and oxygen can only be due to a chemical reaction, *i.e.* the dissolution of aluminium by the sulphuric acid.
3. An excess of oxygen corresponding to the excess of hydrogen is determined as a portion of the aluminium sulphate present in the electrolyte.	
4. The film is soluble in acids and alkalies.	
5. The analysis of the film is on an average : Per cent. Al_2O_3 . . . . 69·8 SO_3 . . . . 13·2 H_2O . . . . 14·8 SiO_2 . . . . 2·2 ——— 100·0	On the basis of the corresponding molecular weights the composition is as follows : $1SO_3 : 5H_2O : 4Al_2O_3$.
6. For constant current density (1 amp./18·84 cm.² = 5·3 amp./dm.²) equal quantities of aluminium are dissolved anodically in equal times.	Note the high current density of 5·3 amp./dm.²

solutions, the current conduction must also be rendered more difficult, and in support of this he drew attention to the fact that the neutral salt solutions used in Pollak's process for rectifiers had proved more suitable than the sulphuric acid originally employed by Graetz.   In spite of the valuable contributions which Norden made to the subject, his aim of explaining the rectifier effect by investigating the chemical processes at the aluminium anode and by analysing the film formed was not achieved.

[1] *Cf.* Table XVII, No. 4.

E. Lecher has provided an interesting contribution to our knowledge of the processes at the aluminium anode. His investigations complete the observations made by Wilson[1] at about the same time on the influence which heating the anode has on the resistance of the oxide film, and hence on the current relations. Lecher used a 10 per cent. potash alum solution as electrolyte, and he employed electrodes of platinum and aluminium. He called the current direction in which the aluminium is cathode the *normal*, and the opposite direction, in which the aluminium is anode, the *critical* direction.[2]

In contradistinction to L. Graetz[3], Lecher found that a sensitive galvanometer always gave evidence of a current in the reverse direction, the magnitude of this current being admittedly in many cases far below the current intensity in the forward direction. He used for his measurements an accumulator battery of 30 cells. The resistance of the measuring circuit, including that of the ammeter and electrolyte, amounted to only a few ohms and could be neglected in comparison with the large resistance of the oxide film in the reverse direction. Lecher remarks, regarding Graetz's conception of the existence of a counter force of 22 v., " No opposing force, except the small amount due to ordinary polarization, exists." The condenser effect of the film is, according to Lecher, due to the high resistance, and is an obvious consequence thereof.

Lecher called the quotient of the forward current over the reverse current the *critical ratio* :

$$\frac{\text{Forward current}}{\text{Reverse current}} = \textit{rectifying ratio} \text{ or critical ratio.}$$

If a small voltage, of the order of 2·0, is applied, the ordinary polarization may conceal the direction of the phenomenon, so that the critical ratio may be even smaller than 1. Lecher, therefore, commenced his investigations with voltages of the order of 10. The surface of each electrode was 1300 cm.[2] He first arranged the current to flow in the forward direction, obtaining a certain current ; on reversal the current was maintained at full strength (1·80 amp.) in the first instant in the reverse direction, but subsequently decreased

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[1] See p. 74.

[2] The frequently used terminology " anodic " and " cathodic " direction of the current is misleading, since the direction of the positive current, *i.e.* the direction from the anode to the cathode, is always understood to be the direction of the current (for solid and liquid conductors). There can, therefore, be no question of " anodic " and " cathodic " current direction, even if by these terms it is understood that the aluminium electrode is made either the anode or the cathode. In the present monograph, we shall denote the current direction in reference to the valve metal by the following terms, which are those usually employed in the literature :

Valve Metal acting as Anode.   Valve Metal acting as Cathode.
    Rectifying direction.   *Normal* direction.
    Reverse direction.   *Forward* direction.

[3] *Cf.* p. 74.

with time, as the following figures show, approaching a constant value :

After . . .	0·1	0·25	0·5	1	3	20	36 min.
Current in reverse direction . .	1·80	1·00	0·80	0·50	0·29	0·18	0·17 amp.

Fig. 18 shows the course of the variation in current in relation to time.

The same phenomenon is observed if an aluminium wire is used as anode, but in this case the current density is greater, so that the end state is reached much more rapidly. In other words, the end state is reached when equilibrium is achieved between the oxide formed in unit time by the current and that which is redissolved. This
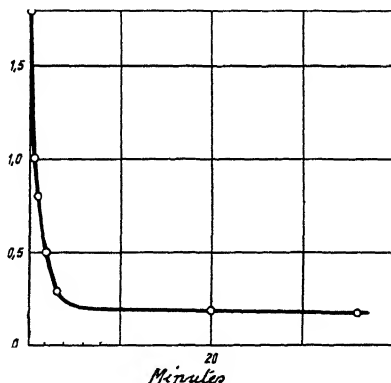

FIG. 18.—Variation of Current with Time at Constant Voltage of 10 in 10 per cent. Potash Alum Solution.

continuous dissolution and re-formation of the oxide film during the passage of the current in the reverse direction is demonstrated by the fact that the rectifying effect is gradually lost once the circuit is opened. The aluminium electrode formed in the above example for 36 mins. (until a permeability of 0·17 amp. was attained) was left in the electrolyte for a long time without current. After an hour the amperage was already 1·12, and after 10 hours it had re-attained 1·70 in the reverse direction, which was the value before forming, a proof that the oxide film had completely disappeared.

The rectifying ratio in the above example of 1·80 to 0·17 is not constant; it increases after the aluminium electrode has been in use for some time. After a large number of alternations of the current direction and several days' use of the electrode, the ratio had increased to 1·80/0·0116, since the forming had not been completed under the given conditions after 36 mins. The figures

given in the following experiments are, therefore, intended to be taken only as comparative values, and not as absolute or accurate determinations of the rectifying ratio.

In the following experiment Lecher used a cathode of 45 cm.^{2} surface, which was employed in one case with an aluminium sheet of equal magnitude, and in another case with an aluminium wire 1 mm. thick. The wire was immersed 1 cm. in the electrolyte, *i.e.* it had an effective surface of only 0·3 cm.^{2} The rectifying ratio at different voltages (10 and 20) was determined initially, the distance between the electrodes being so chosen that the current in the forward direction in both experiments was as nearly as possible equal. After forming, the current was reversed to the forward direction. In order to obtain the same current in this direction as

<div align="center">TABLE XVIII</div>

Experiment No.	Applied Voltage, approx.	Surface-area of Aluminium Electrode, cm.^{2}	Distance between Electrodes, cm.	Rectifying Ratio.	Resistance necessary in Forward Direction, ohms.
1	10	45	0·5	$\dfrac{2\cdot00}{0\cdot01}$	880
2	20	45	> 0·5	$\dfrac{2\cdot10}{0\cdot047}$	350
3	10	0·3	—	$\dfrac{0\cdot43}{9 \cdot 10^{-6}}$	900,000
4	20	0·3	—	$\dfrac{1\cdot25}{8 \cdot 10^{-5}}$	110,000

in the reverse direction, a certain resistance was required, and Lecher took this as a measure of the resistance of the oxide film in the reverse direction.

The results of these experiments are shown in Table XVIII.

With the higher voltages of 20 (experiments 2 and 4) the resistance necessary to balance the currents in the two directions is considerably smaller than with 10 v. (experiments 1 and 3). Lecher attributed this difference to the greater heating of the oxide film due to the greater final current density in the reverse direction; and he accounted for the high resistance of the wire anode by the large initial current density due to the small surface and the consequently more rapid forming.

The experiments of Lecher's described up till now are to be taken merely as generally informative, and it must be appreciated that no accurate data are given regarding the purity of the

aluminium, the temperature and quantity of the electrolyte, the period of forming, and of the cathodic treatment of the aluminium.

On raising the voltage applied to the aluminium cell to 30 and over, the oxide film becomes very hot. Lecher used as anode a hollow aluminium cylinder having walls about 0·5 mm. thick, which just fitted over the reservoir of a mercury thermometer. When the applied voltage reached 40 and a current of 0·9 amp. was registered, the temperature rose to 80° C., and at 60 v. and 4·0 amps. to 105° C., the mercury thread rising as suddenly as if the thermometer had been plunged into hot water ; in fact the heating took place almost instantaneously. When the current was reversed to the forward direction the thermometer registered an almost equally rapid fall of temperature, although the current was in this case much greater. At the above-mentioned temperature the liquid in the immediate neighbourhood of the anode boiled. This means that the anode coating itself must have been yet hotter than was indicated by the thermometer, since the electrolyte must have had a cooling effect. When the wire formed at 60 v. was observed under the microscope after removal of the film, it appeared almost as if melting of the surface had taken place.

In support of the view that the rectifying ratio for high voltages is varied by the heating of the aluminium anode and approximates to the value unity, Lecher carried out the following interesting experiment : a closely fitting spiral of 0·5 mm. thick aluminium wire was wound round the mercury reservoir of the thermometer, the aluminium serving as anode. When voltages of 40 to 60 were employed the same phenomenon of rapid rise of temperature was observed, although in consequence of the considerable cooling due to the electrolyte the actual rise was less than in the preceding experiment. At 10 v. the thermometer no longer exhibited any rise of temperature. If, however, a separate heating current was conducted through the anode spiral the rectifying effect suddenly disappeared after a certain degree of heating had been reached, as can be seen from the following example. Initially, the current in the forward direction was 0·81 amp. and that measured in the reverse direction was 0·0002 amp. If a heating current of 40 to 50 amp. was sent through the spiral the reverse current reached the same value as the forward current. This proves that the resistance of the anode coating is reduced by heating the anode.

The supposition that the amount of heating required to reduce the rectifying ratio to unity must be very great is supported by the actual magnitude of the heating current of 40 to 50 amp. Such currents can pass for only a brief instant through the thin wire, since the wire, already attacked by the electrolysis, rapidly melts in spite of the cooling which the electrolyte affords. Since in this case it is necessary almost to melt the aluminium in order to bring

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the reverse current to the level of the forward current (ratio = 1), it follows that the anode must be very strongly heated by the direct effect of high voltages also.

In a further series of experiments Lecher investigated the influence of the voltage on the rectifying ratio, using in one case a large and a very small aluminium electrode, and in the other case a circuit with and without a resistance. The platinum electrode of 1300 cm.^{2} surface was used either with an aluminium anode (sheet form) of equal area, or with an aluminium wire 1 mm. in thickness of about 0·5 cm.^{2} effective surface (point electrode).

TABLE XIX

Voltage.	Rectifying Ratio in Circuit of Total Resistance (without Cell Resistance)			
	Approx. 4.5 ohms.		Approx. 90 ohms.	
	Sheet Electrode.	Point Electrode.	Sheet Electrode.	Point Electrode.
10·2	$\dfrac{1·92}{0·012} = 142$	$\dfrac{0·35}{1·6 \cdot 10^{-5}} = 22{,}000$	$\dfrac{0·091}{0·012} = 7·9$	$\dfrac{0·06}{1·6 \cdot 10^{-5}} = 3{,}750$
20·3	$\dfrac{4·20}{0·06} = 70$	$\dfrac{1·25}{8 \cdot 10^{-5}} = 15{,}600$	$\dfrac{0·22}{0·04} = 5·5$	$\dfrac{0·17}{8 \cdot 10^{-5}} = 2{,}160$
31·2	$\dfrac{6·7}{0·4} = 17$	$\dfrac{1·7}{0·0012} = 1{,}400$	$\dfrac{0·32}{0·09} = 3·5$	$\dfrac{0·28}{6 \cdot 10^{-4}} = 467$
41·6	$\dfrac{8·9}{1·6} = 5·5$	$\dfrac{2·0}{0·5} = 4·0$	$\dfrac{0·45}{0·15} = 3·0$	$\dfrac{0·40}{0·08} = 5·0$
51·8	$\dfrac{11·2}{3·5} = 3·2$	$\dfrac{2·5}{1·6} = 1·6$	$\dfrac{0·57}{0·25} = 2·3$	$\dfrac{0·46}{0·11} = 4·2$
62·0	$\dfrac{13·0}{6·1} = 2·1$	$\dfrac{3·0}{3·0} = 1·0$	$\dfrac{0·69}{0·39} = 1·8$	$\dfrac{0·55}{0·29} = 1·9$

The total resistance of the circuit without the cell resistance amounted in the one series of tests to about 4·5 ohms and in the other to about 90 ohms. The values thus derived are collected in Table XIX.

The left-hand side of the table, corresponding to the small resistance of the circuit, shows that for small voltages (10·2) the rectifying ratio for the sheet electrode is small (142) in comparison with that for the point electrode (22,000). This is connected with the fact that in the latter case the current density (0·7 amp./cm.^{2}), and hence the film thickness, are considerably greater than in the former (0·0014 amp./cm.^{2}). At the higher voltages, e.g. 62 v., the heating of the wire electrode is so strong that it is no longer possible to speak of a resistance of the oxide film, whilst the sheet electrode is still able to reduce the current to half the value in the forward direction.

The right-hand side of the table shows, in the first place, that the external resistance in the circuit reduces the effect of the anode resistance. The rectifying ratio for low voltages is smaller than when no resistance is included in the circuit. For larger voltages, however, the heating up of the anode is reduced, since part of the potential drop is taken up by the circuit resistance, and in this case the inclusion of a resistance tends to increase the rectifying ratio of the small wire electrode; *e.g.* for 51·8 v. the value 1·6 is obtained without resistance, and when the resistance is included the ratio is 4·2.

Wilson[1] arrived at a similar result, as has already been mentioned, regarding the effect of temperature on the current strength in the reverse direction in an aluminium cell. He concerned himself, however, with the temperature of the electrolyte, and he showed *inter alia* that with saturated potassium alum solution a rise in temperature from 13·5° to 70° C. brought about a fall in the voltage from 30 to 3, the current being maintained constant. In this connection he pointed out that, in practice, to obtain a high resistance of the oxide film, the electrolyte must be cooled or kept in motion.
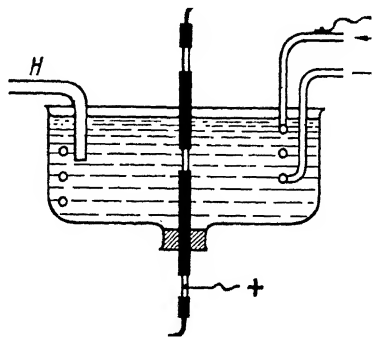

FIG. 19.—Device for the Internal Cooling of an Aluminium Anode.

In connection with these investigations regarding the influence of temperature on the formation of the film, some researches carried out by F. Fischer in the year 1904 are of interest. Fischer showed that there is a limit for an electrolyte at room temperature above which the voltage cannot be increased without destroying the rectifying effect of the aluminium anode. He named this limiting value the *inversion point*.[2] On the other hand, the voltage can be increased to high values if the electrolyte is kept at a low temperature and the aluminium tube used as anode is simultaneously cooled internally. The experimental arrangement which Fischer developed is shown diagrammatically in Fig. 19, in which the aluminium tube, the greater part of which is surrounded with insulating material, is shown in the middle of the vessel. A lead coil was used as cathode and served at the same time to cool the electrolyte. The siphon *H* led to a reference electrode, which served for measuring the potential difference between the liquid and the aluminium anode.

The course of the current and of the voltage in relation to time, as determined by F. Fischer, is shown in Fig. 20. The current curve shows the typical falling off of the current immediately after the

[1] *Cf.* pp. 74 and 78.   [2] *Cf.* p. 94, " Maximum Voltage."

circuit is closed which has already been referred to. The uniform course of the current curve was not affected by the raising of the voltage carried out by Fischer at certain time intervals, if the momentary small current impulse after each increase in voltage is neglected.[1] It is worthy of note that due to the internal cooling of the anode it was possible to attain film thicknesses of several tenths of a millimetre.

The next stage of interest was the preparation of the surface of aluminium in order to provide a good basis for the adhesion of paints and lacquers, and the so-called colouring of the metal. Numerous chemical processes have been proposed with these objects. The first attempts to produce protective films electrolytically used sodium phosphate solutions. In 1907 came the first of the attempts
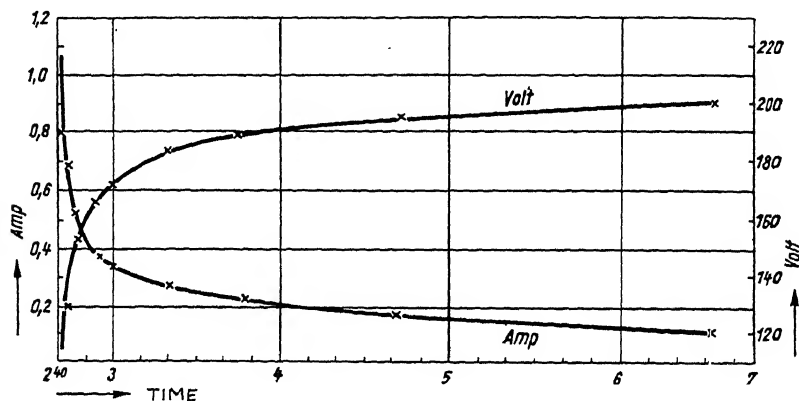
FIG. 20.—Curves showing the Variation of Current and Voltage with Time during the Anodic Oxidation of Aluminium.

to produce electrically insulating films, in some cases chemically (F. Singer, 1908) and in others by means of anodic oxidation (L. W. Chubb, 1907). A large number of investigations were also carried out in the attempt to deposit aluminium compounds cathodically from aluminium salt solutions. A proposal by J. Vogelsanger (1913) to render aluminium resistant by electrolytic treatment in an aqueous solution of alum, borax and caustic potash was completely overlooked in technical circles. It was not until 1923 that the process developed by G. D. Bengough and J. M. Stuart drew the attention of interested circles to the possibility of effective corrosion-protection of aluminium and its alloys by means of anodic treatment. The protective films produced by this process can be coloured with organic dyestuffs. Parallel with these attempts to attain the desired end electrolytically, investigations were carried out to produce effective protective films

[1] *Cf.* p. 99.

by purely chemical methods. Numerous patents, both in Germany and other countries, were taken out in this connection, but the films produced chemically, in spite of the advantages in production, could not compete with those produced anodically.

Simultaneously with the work carried out in connection with commercial development, scientific research on the subject received a strong impetus, and theoretical discussion of the mechanism of the phenomena at the valve anode was extended. Much light has been thrown on the nature of these phenomena. Nevertheless, there is, as yet, no complete explanation of the singular phenomenon of unipolar conduction.

Summary of the Results of the Historical Survey

In the foregoing summary a large number of important phenomena observed at the aluminium anode have been noted. The most important of these will be briefly summarized in the following :—

1. The valve effect, or rectifying effect, *i.e.* unidirectional or unipolar conduction in electrolytic cells, has been observed to a small extent in the case of iron, as well as with aluminium. The current flows unhindered in the direction in which the valve metal behaves as cathode, but in the opposite direction, in which the valve metal is anode, it meets a high resistance, which allows only a fraction of the current observed in the forward direction to pass. The use of the aluminium cell as a rectifier is based on this property.

2. The oxide film which forms on the aluminium anode when the current passes is responsible for the valve or rectifying effect. The effect is not that of an ordinary ohmic resistance, for which the current direction is of no importance. Other factors must contribute to this behaviour. The researches which have been carried out up to the present have not allowed of a completely satisfactory explanation of this singular phenomenon.

3. The following electrolytes have been described as suitable for the aluminium valve cell :

Aqueous solutions of :
  Potassium alum,
  Neutral or alkaline phosphates,
  Bicarbonates of the alkali metals or ammonium,
  Ammonium borate,
  Salts of dibasic organic acids,
  Salts of hydroxy acids, aldehydic acids and ketonic acids,
  Weakly acidified organic magnesium or aluminium salts,
  Magnesium or calcium bicarbonate,
  Mandelates of the alkaline earth or earth metals,
  Acidified organic ammonium salts.

The rectifying effect has also been observed in sulphuric acid.

4. No rectifying film is formed in hydrochloric acid or in chloride solutions.

5. Of the electrolytes containing oxygen-bearing anions differentiation should be made between those which have a moderately solvent effect on the film once it is formed, such as dilute sulphuric acid, and those which have no solvent action. Every intermediate stage of solubility is conceivable.

6. The aluminium anode behaves as a condenser whose dielectric is formed by the oxide film, and whose two plates or electrodes consist of metallic aluminium on the one hand, and of the electrolyte on the other hand.

7. Using a standard forming process for the aluminium anode, with a current source of suitable constant voltage, the initially heavy current density rapidly falls off, to approach, as the treatment is continued, a constant final value, whose magnitude depends, other factors being equal, on the applied voltage.

8. At the final stage of forming, equilibrium is reached between the formation and the dissolution of the film.

9. After the equilibrium condition is reached, there is always a measurable current in the rectifying direction, even though this may be very small in relation to the initial current density. This final current in the reverse direction is called the *leakage current*.

10. During the formation of the film the aluminium anode undergoes heating. This heating is small so long as the velocity of film-formation (the forming or formation velocity), which is dependent on the applied voltage or the current density at the anode, is small. As the voltage or the current density increases the temperature of the anode rises. The heat taken up by the anode is transferred to the electrolyte, which must be cooled in order to oppose the increasing solvent effect of the electrolyte on the film as the temperature rises, and the consequent diminution or discontinuance of the valve effect.

11. If the valve metal once formed is allowed to remain in electrolytes which have a solvent effect on the film, even with no current, the film is dissolved after a certain time.

12. The oxide film on aluminium is attacked by alkalies and acids.

13. The natural oxide coating which is always present on aluminium protects the metal, which in itself is highly electropositive, from further attack by atmospheric oxygen, and imparts to it a more electronegative character than its own electrochemical properties bestow on it.

14. The forming velocity of very small aluminium anodes (point electrodes) is greater, other conditions being equal, than that of larger aluminium anodes (sheet electrodes), as a result of the heavy current density at the point electrodes.

15. The film which forms on the aluminium anode consists essentially of hydrated aluminium oxide.

16. Initially the attempts to make technical or commercial use of oxide films produced anodically on aluminium were confined to the applications to electrolytic rectifiers and condensers ; it was only later on that interest was taken in those fields of application which depend on a knowledge of the protective effect of oxide films against mechanical and corrosive influences.

Valve Metals

The valve effect which has been observed on aluminium and, to a small extent, on iron[1] may also be found in connection with quite a number of other metals. These are enumerated in the following, together with information regarding the electrolytes in which the rectifying effect occurs. The majority of the data are taken from A. Güntherschulze's work on the subject.

Tantalum.—Forming is considerably more rapid than with aluminium ; the barrier effect occurs in all the electrolytes which have been investigated up to the present, including potassium hydroxide and potassium carbonate, but it does not occur in hydrofluoric acid.

Niobium.—Caustic soda, potassium carbonate, ammonia, ammonium phosphate, sodium bromide, potassium iodide, hydrofluoric acid, hydrochloric acid, sulphuric acid, nitric acid, arsenic acid, acetic acid, potassium permanganate, diammonium phosphate, sodium bromide, potassium iodide, potassium dichromate. Behaves in the same way as tantalum.

Vanadium.—Behaves similarly to niobium and tantalum.

Antimony.—In almost all electrolytes : acids, bases, salts ; highest voltage (700) may be used in very dilute potassium chloride solution.

Bismuth.—In almost all electrolytes, as for antimony ; highest voltage (600) attainable in very dilute potassium hydroxide solution.

Magnesium.—Potassium hydroxide, potassium carbonate, disodium phosphate, ammonia, fuming sulphuric acid.

Zinc, cadmium.—Marked valve effect in potassium carbonate solution. Fuming sulphuric acid.

Iron.—Fuming sulphuric acid ; only passivity occurs in sulphuric acid below 50 per cent. ; 60 per cent. and over valve effect occurs,

[1] P. 71.

but this is unstable up to 75 per cent. With higher concentrations the valve effect is permanent (40 to 70 v.).

Nickel, cobalt.—Behave in the same way as iron; valve effect in fuming sulphuric acid.

Copper.—In aqueous hydrofluoric acid, copper sulphate, copper chloride; in fuming sulphuric acid at high current densities.

Silver.—In hydrochloric acid, hydrobromic acid and hydriodic acid; formation of silver halides.

Lead.—In 1 per cent. and in fuming sulphuric acid; formation of lead sulphate.

Tin, tungsten, chromium.—Show no marked valve effect.

Cerium.—In borax solution, also with A.C.

Titanium.—In borax solution.

In addition to the above metals, the valve effect has also been observed with beryllium, uranium and zirconium.

Aluminium.—Valve action occurs in:

> Acids—chromic, sulphuric, boric, di- and tribasic organic acids (oxalic, malonic, succinic, citric); in 45 per cent. or very dilute phosphoric acid, valve action occurs, but is not fully developed.

> Salts—acid and neutral sulphates (potash alum), phosphates (sodium metaphosphate, disodium phosphate), borax, sodium bicarbonate, ammonium borate, ammonium carbonate, soap solution, potassium dichromate, water-glass. The valve effect does not occur, or occurs only incompletely, in alkalies, halogen salts, nitrates, halogen acids, monobasic organic acids (formic acid, acetic acid), dilute phosphoric acid, nitric acid (5-10 per cent.). In concentrated nitric acid at 30° C. regular variations in the voltage, and gas evolution occur. The metal surface remains apparently unchanged.

The analogy between the chemical and the anodic behaviour of aluminium is clear from the above survey.[1] In both cases there are all the gradations between complete solubility and almost complete insolubility of the aluminium or aluminium anode, or of the oxide film formed on it. From researches which have been carried out with aluminium anodes up to the present, it is clear from their behaviour towards free acids that film formation either does not occur or occurs only very incompletely in aqueous monobasic acids, whether they are inorganic or organic.

[1] *Cf.* also the summary given on pp. 55-65.

Classification of Metallic Anodes according to the Properties of the Compounds which form at them[1]

, In regard to the properties of the compounds which are formed at metallic anodes in any given electrolyte the following cases may be differentiated :

I. The anode forms no compound with the anion or with part of the latter, and does not go into solution. *Example* : Platinum in acids or salts containing oxy-anions, and in bases.

II. The anode forms only readily soluble compounds with the anion or with part of the latter. *Example* : Aluminium in solutions of the halogen salts, in dilute nitric acid, or in monobasic organic acids.

III. The anode forms difficultly soluble or insoluble compounds with the anion or with part of the latter and becomes covered with a coating of the compound in question. This case may be further subdivided into two :

(A) The coating adheres only loosely to the metal ; it is pulverulent, spongy, or coarsely porous :

(i) It conducts the electric current. It then protects the metal from the attack of the anion, the better the more coherent and the thicker it is. *Example* : Lead in sulphuric acid.

(ii) It does not conduct the electric current. In this case it cannot protect the metal from further attack by the anion. The current will progressively thicken it until it begins to peel off from the metal. *Example* : Lead in chromate solution.

(B) The coating adheres firmly to the metal and forms a cohesive film.

(i) The film conducts the electric current ; it then protects the metal from further attack by the anion (so long as the anion does not secondarily diffuse through it) and remains of molecular thickness. The metal has become passive. *Example* : Iron in aqueous sulphuric acid below a concentration of 50 per cent.

(ii) The film does not conduct the electric current. In this case the anions penetrate the film when the voltage is sufficiently high. The film has

[1] Based on A. Güntherschulze's work.

a fine-pored structure; it is permeated by microscopic capillaries and can grow to greater thickness in proportion to the effective conductivity of the total cross-section of the pores.

(a) If the film is practically insoluble in the electrolyte, the pore cross-section remains unchanged. As the film thickness increases the resistance in the pores is augmented, until the current falls to such a small value that the growth is in practice largely prevented and finally comes almost to a standstill. In the non-solvent electrolytes, therefore, extremely thin and fine-pored films are obtained and the valve effect achieved is complete. The non-solvent electrolytes find extensive application in the electrolytic condensers used by the wireless industry.

(b) If the film is appreciably soluble in the electrolyte, the cross-section of the pores gradually increases. This means that the total cross-section of the pores is augmented, and the resistance in them is reduced to such a point that sufficient current for the further growth of the film can reach the metal. In this case the valve effect obtained is incomplete. The film grows until equilibrium is arrived at between formation and dissolution by the electrolyte. After this point is reached, virtually no further increase of the film thickness is effected, though the film may penetrate progressively deeper into the metal. *Example* : Aluminium in the electrolytes used commercially for the production of thick films.

Every gradation between the limiting cases described in (a) and (b) is possible, according to the solubility of the film. As the solubility of the film increases above the case discussed in (b) the thickness of the film decreases. Where the oxidation product is readily soluble no further film can form ; the case then becomes that described under II.

Cathodic Behaviour of Aluminium

In connection with the production of protective films the cathodic behaviour of aluminium is not of the same order of interest, and it will merely be mentioned that the existence of the natural oxide skin on aluminium and its alloys gives rise to great difficulties in connection with the electrodeposition of metals, since the metal deposits do not adhere to the oxide surface on the aluminium cathode. Recently processes have been developed which, by means of suitable anodic pretreatment, do away with the difficulties due to the natural oxide skin and allow of the formation of adherent galvanic deposits on aluminium.[1]

[1] The " Elytal " process.

CHAPTER VII

THE ANODIC OXIDATION OF ALUMINIUM

THE considerations discussed up to the present on the formation of oxide films on aluminium have been limited to direct current treatment and to the most prominent phenomena, and we have not gone into the mutual relationship between the different factors which play a part in the processes concerned. We shall consider these relationships in some detail in the following in so far as they affect the production of protective films, and we shall further discuss some of the phenomena observed in connection with the alternating current treatment of aluminium.

A.—Direct Current Treatment
Current/Time Curves and Voltage/Time Curves
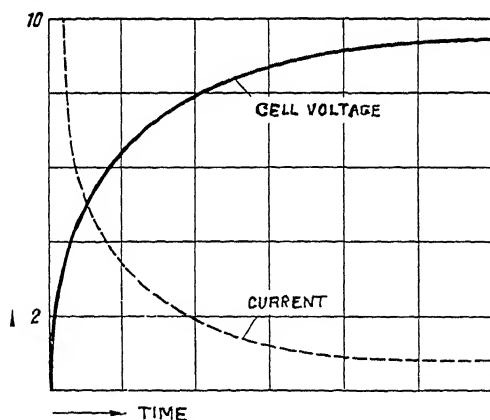
FIG. 21.—Diagrammatic Representation of Variation of Current and Voltage with Time during the Forming of an Aluminium Anode using D.C. without a Series Resistance.

When a direct current of 10 v. is applied to a cell containing a suitable acid solution and provided with an aluminium anode the current initially falls off rapidly and subsequently more slowly until it approaches a constant value (*cf.* Fig. 18, p. 79). As long as no external resistance is used the voltage drop in the cell is principally determined by the resistance of the electrolyte, which ultimately becomes small in comparison with that of the oxide film,

which grows on the aluminium anode with time.   Accordingly, the terminal voltage is small immediately after the circuit is closed, but this increases, as the resistance of the film progressively grows, in accordance with Ohm's law.   The current and voltage may be
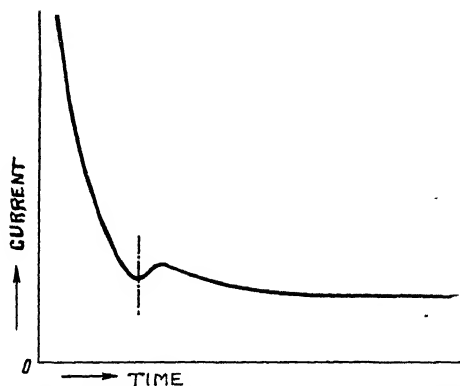

FIG. 22.—Current/Time Curve at Constant Voltage.[1]

measured and plotted against time, giving the curves in Fig. 21. The voltage and the current in the cell, when oxidation is carried out without an external resistance, are automatically adjusted by the resistance of the anode in the rectifying direction.
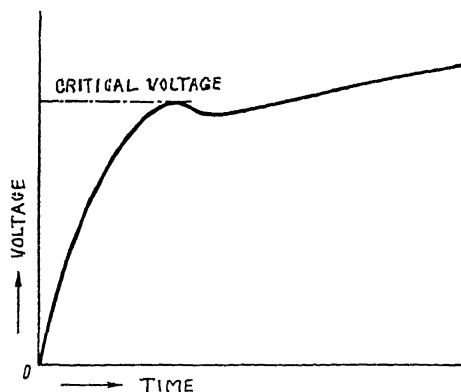
FIG. 23.—Voltage/Time Curve at Constant Current.[1]

If an external resistance or a rheostat is inserted in the circuit, the voltage or the current may be maintained constant. In this way current/time curves may be obtained for a given voltage or voltage/time curves may be derived for any current density. Such curves are shown in Figs. 22 and 23[1].

[1] S. Setoh and A. Miyata.   Frequent reference is made in the following paragraphs to the work of these authors.

The current/time curve shown in Fig. 22 has a minimum in the neighbourhood of the dotted line. This minimum can be accurately determined at low voltages since the variations in current in this case are small. The rapid rise of voltage necessary to maintain a constant current may be seen in Fig. 23. After a certain value, known as the *critical voltage* or *maximum voltage*, is attained, further rise of voltage occurs only slowly.
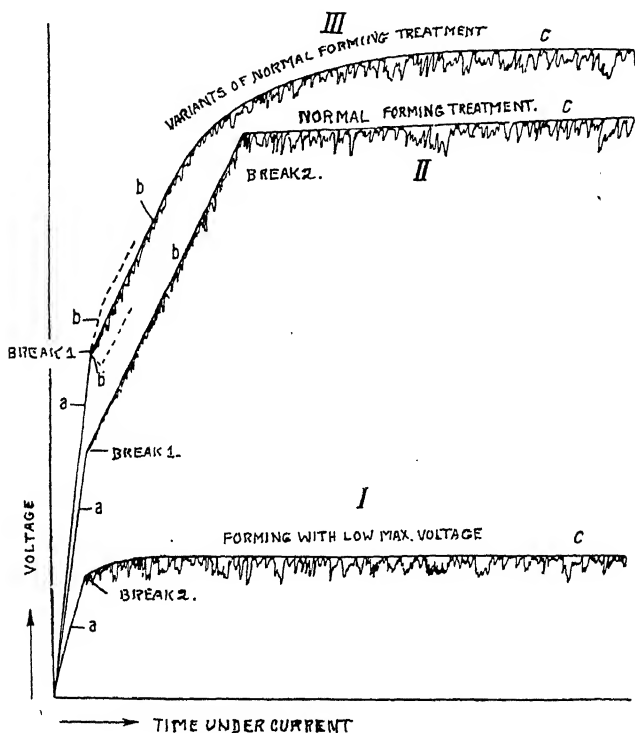
Spark Voltage : Maximum Voltage

FIG. 24.—Spark Voltage (*b*) and Maximum Voltage (*c*).

A. Güntherschulze found that when forming with constant current density, the increase in the bath voltage is initially approximately proportional to the period during which the current operates, until at a definite voltage small sparks suddenly appear at the surface of the valve anode (Fig. 24, curve II, break 1). From this instant the cell voltage rises more slowly, but still linearly. The sparks become gradually more brilliant until, when the voltage reaches a second critical value (break 2), sparks associated with a

crackling sound are emitted. After this, the voltage increases only slightly or not at all. The forming process is ended. The voltage on the portion of the curve *b*, from break 1 onward, at which small sparks appear, is known as the *spark voltage*; and the voltage from break 2 onward, along the portion of the curve *c*, which indicates the end of forming, is known as the *maximum voltage*. The fluctuations in the voltage due to the spark discharges are shown diagrammatically in the figure by the zig-zag lines.

The maximum voltage is dependent on the nature and on the concentration of the electrolyte; in the case of monovalent electrolytes, it depends on the concentration of the ions, not on the total concentration. It attains a characteristic value in every electrolyte. In some electrolytes the portion of the curve *b* proceeds, without a break, in a continuous curve into the portion *c*, as is shown in curve III. If the maximum voltage of the electrolyte is less than 150 to 200, in most cases there is only one break and curve I is obtained, in which the spark voltage and maximum voltage coincide.

The spark voltage is dependent on the valve metal and on the nature and concentration of the electrolyte, but it is independent of the temperature and the current density.

In the case of tantalum, which is insoluble in the majority of electrolytes, with the exception of hydrofluoric acid, the maximum voltage attains very high values in most cases. The forming is very similar with aluminium in certain salt solutions, but in others it varies quite markedly from that with tantalum. This is due to the solubility of the aluminium in the electrolytes in question. The solubility increases rapidly as the temperature rises; and the temperature in turn rises rapidly with the forming voltage, even where the cooling of the electrolyte is carried out efficiently. The consequence is that in any electrolyte in which aluminium is soluble to any extent, even before attaining the true maximum voltage there arrives a stage at which the quantity of film dissolved by secondary processes is equal to that which is formed in the first instance by the current. After this the voltage cannot increase further; in other words, an apparent maximum voltage is attained. In cases where this apparent maximum is reached only in the neighbourhood of the true maximum voltage (the aluminium being only very slightly soluble), when a lively spark discharge is present, it is difficult to distinguish between the true and the apparent maximum voltage. Such cases occur with sodium borate, sodium citrate and sodium bicarbonate solutions.

An indication as to whether the true maximum voltage for aluminium has been reached is supplied by comparison with the maximum voltage of tantalum. In all electrolytes in which aluminium is not appreciably soluble, it exhibits approximately the

same true maximum voltage as tantalum ; in all other electrolytes the apparent maximum voltage of aluminium is lower than that of tantalum by an amount which varies directly with the solubility of the aluminium or of the oxide film on the aluminium.

In the latter case, where there is marked solubility of the oxide film in the electrolyte, the fundamental conditions for the production of thick protective films are operative (p. 90). In the commercial processes for anodic oxidation the concentrations of the electrolyte and the working conditions (current density, temperature) are chosen to be such that the film will grow in thickness as rapidly as possible. In these processes, however, the spark voltage or the true maximum voltage is never reached. The bath voltage must be controlled according to the solvent action of the electrolyte in such a way that the anode never heats up sufficiently to raise the temperature of the bath above the limiting value at which the solution velocity is greater than the velocity of formation of the film. The voltage which automatically operates across the bath terminals once the initially high current density has fallen off is, therefore, in all the commercially operated processes, below the spark voltage or the maximum voltage. The latter is only attained if it is necessary progressively to increase the voltage in order to maintain a given current, and there is no question of this in the commercial production of protective films.

Glow Discharge Phenomena at Valve Anodes

In addition to the spark discharge which has been referred to, numerous research workers have also observed another phenomenon, the appearance of a brilliant glow uniformly distributed over the whole anode surface. This glow discharge phenomenon occurs both with direct current and with alternating current, in the latter case being noticeable at both electrodes if both are valve metals. If alternating current is used, and if the electrolyte is very dilute, this glow may be increased to give a comparatively brilliant light before the spark voltage is reached. The glow passes through a series of colours, the initial and end points varying with different metals, and also with aluminium and its alloys. According to H. Betz, the brilliance of the light is reduced if zinc is added to the aluminium ; but it is strongly increased if manganese is added, the degree of brilliance initially increasing rapidly in proportion to the amount of manganese, but rapidly tending to a saturation point. Additions of other metals (Cr, Cu, Fe, Mg) have no influence on the brilliance of the glow discharge.

Betz attributes the glow discharge to the high field strength, of the order of magnitude of 10^7 volt per cm., which may be reached in the oxide film, at which the electrons stream through the insulating

film.   The phenomenon is frequently quoted as an argument in support of the theory that it is not the solid oxide film which is responsible for the unidirectional conduction of the valve anode, but a gas film entrapped in the pores of the film.
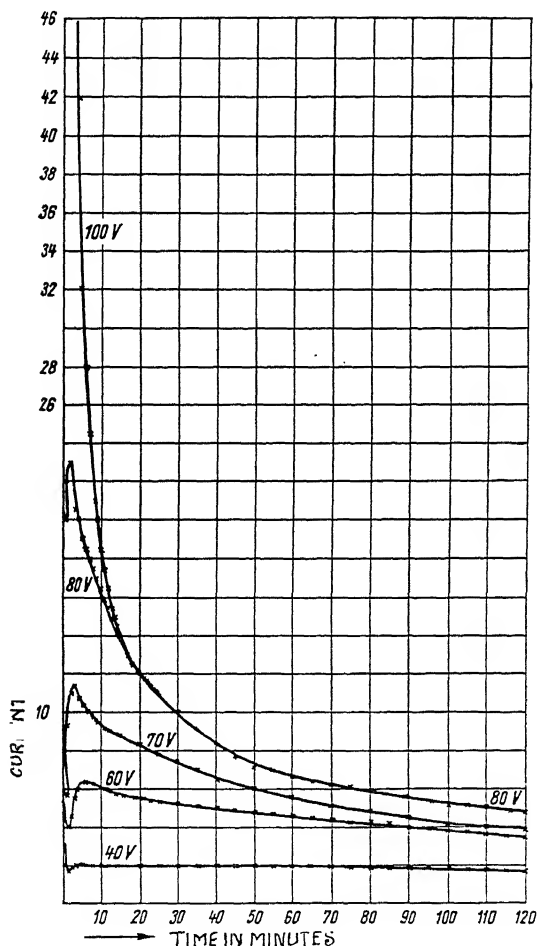
Current/Time Curves at Constant Voltages

FIG. 25.—Current/Time Curves for Different Constant Voltages. Anode surface = 80 cm.²; 17–18° C.

Fig. 25 shows the variation of the current with time for different constant voltages.   The researches were carried out with direct current on aluminium anodes 0·5 mm. in thickness and 80 cm.²

7

in surface area in a 2 per cent. oxalic acid solution (calculated as the dihydrate, $(COOH)_2 . 2H_2O$.[1] The electrolyte was agitated by means of compressed air, and the temperature was maintained at 17° to 18° C. by means of a cooling coil. The bath voltages employed were 40, 60, 70, 80 and 100, respectively.

As the bath voltage was increased both the initial amperage and the leakage current increased, so that with increasing voltage the curves were shifted in position towards larger currents.
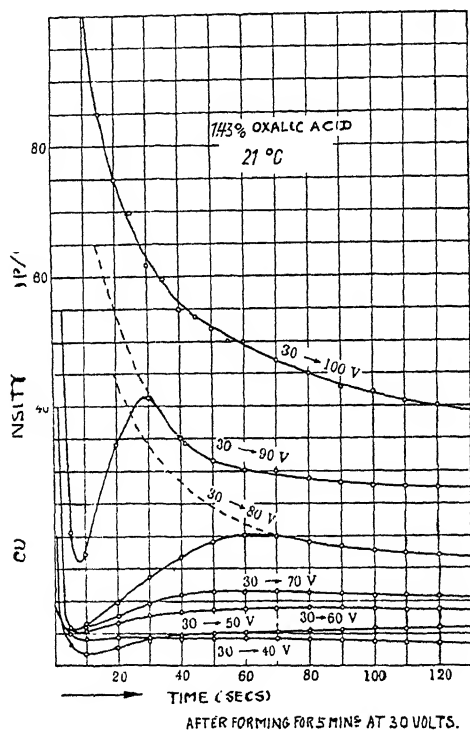
FIG. 26.—Current/Time Curves after Sudden Raising of the Voltage during Forming at 30 volts.

[1] This corresponds to a content of 1·4286 per cent. of anhydrous acid.

N.B.—It is usual, and scientifically correct, to give the percentage content of a solution in reference to the anhydrous substance. Thus the percentage content of a solution in which a given quantity in grams of hydrated oxalic acid is dissolved has to be calculated on the basis of the ratio of the molecular weights, i.e. $C_2O_4H_2 : C_2O_4H_2 . 2H_2O = 90 : 126 = 5 : 7 = 0.71$. A solution which contains 2 g. of hydrated acid per 100 cc. is therefore $2 \times 0.71 = 1.42$ per cent. Conversely, it is possible to calculate how much hydrated acid is necessary in order to arrive at a 5 per cent. solution by multiplying by the factor $126 : 90 = 7 : 5 = 1.4$; i.e. $5 \times 1.4 = 7$ gram hydrated oxalic acid per 100 cc. of water. In the following the percentage content of oxalic acid solutions will always be given in terms of anhydrous oxalic acid ($C_2O_4H_2$) unless otherwise stated.

Current Density/Time Curves after Sudden Voltage Changes

If during forming the bath voltage is suddenly increased a certain amount, the current immediately rises, to a greater or lesser extent, and then rapidly falls off again until it reaches a minimum value, after which it rises again and gradually approaches the normal value for the new conditions. Figs. 26 and 27 show examples of current density/time curves obtained after sudden increase in voltage during the anodic forming of aluminium in
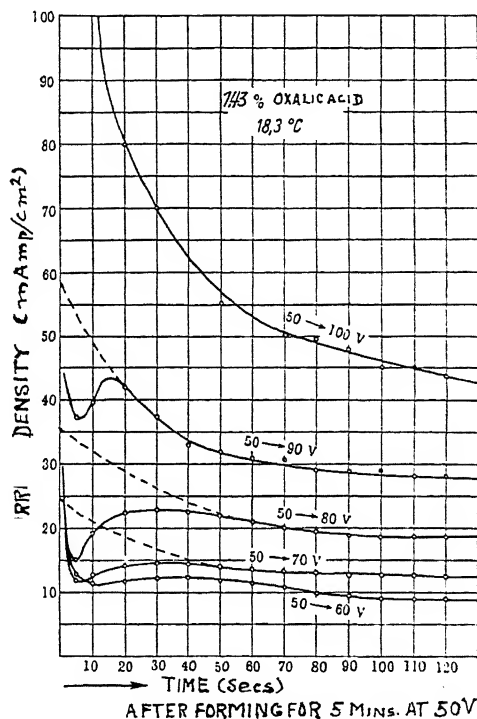
FIG. 27.—Current/Time Curves after Sudden Raising of the Voltage during Forming at 50 volts.

1·43 per cent. aqueous oxalic acid solution at room temperature. In the one case forming is carried out at 30 v., and in the other case at 50 v. After 5 minutes' forming the respective voltages were raised in the first place to 50, 60, 70, up to 100, and in the second case to 60, 70, 80, etc. Nearly all the curves show the sudden rise after the increase in voltage and some seconds later show a minimum value, after which they reach the normal state corresponding to the higher value of the suddenly increased voltage. If the sudden increase of voltage is only small the normal curve is reached only slowly.

If the voltage is suddenly decreased during forming the current also decreases for a while almost to zero, and then rises gradually to approach a constant value. Fig. 28 shows the course of the current density/time curves where the voltage is suddenly dropped after about 10 minutes' electrolysis at 100 and 50 respectively. Where the voltage is suddenly lowered the current falls off, the ammeter needle remaining in the neighbourhood of the zero position. After some time the current attains its normal value.

M. E. Meserve has investigated the relationship between the current i and the time, using different aluminium surfaces and different constant voltages E in a 20 per cent. sodium bicarbonate solution, in which the anodically formed aluminium oxide is
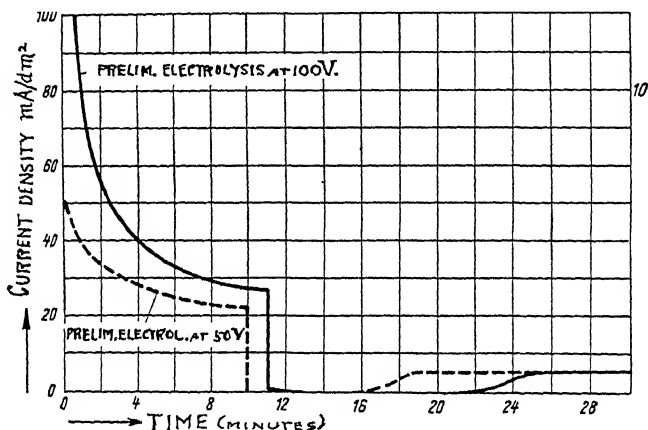
Fig. 28.—Current Density/Time Curves obtained by suddenly decreasing the Voltage during Forming at 50 and at 100 volts in Oxalic Acid.

practically insoluble. The following results are of importance for our considerations :

(1) After a lag of more than 300 seconds, the resistance of the cell increases linearly with the quantity of electricity passed through it.

(2) The thickness of the film increases linearly with the resistance of the cell, and hence with the quantity of electricity which has passed through the cell (cf. Fig. 29).

Current/Time Law

It has also been shown by Meserve that in the electrolyte which he used ($NaHCO_3$) almost the whole of the oxygen discharged at the anode (viz. 96 per cent.) combines with the aluminium to form

the solid film. According to Meserve, for constant voltage E, the square of the current i is inversely proportional to the period of forming t provided t is not less than 300 seconds. This means that the law only applies after a lag of at least 300 seconds from the instant of switching on the current. The expression :

$$\frac{E}{i^2} = Ct + D$$

represents a straight line in which C is the slope of the line with respect to the horizontal axis and D is a constant. This fact has been experimentally confirmed by W. J. Müller and K. Konopicky, and is in agreement with Müller's time law for film passivity, in
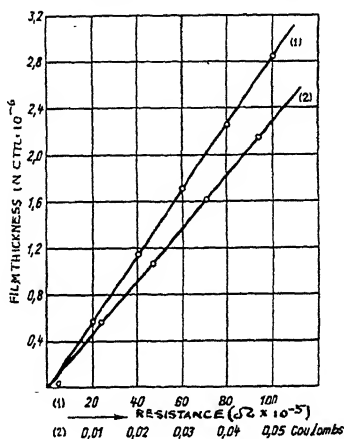
FIG. 29.—Linear Variation in Film Thickness with (1) Resistance of Cell and (2) Current Expenditure.

accordance with which the current i, where the voltage is maintained constant, initially rises rapidly and then falls off in accordance with the $1/i^2$ law.

Voltage/Time Curves at Constant Currents

Setoh and Miyata have determined the rise in voltage necessary to maintain the current constant, in a series of investigations in which the influence of the concentration and temperature of the electrolyte on the voltage was also determined. They used as electrolyte a 1·43 per cent. oxalic acid solution and as cathode an aluminium sheet 5 × 5 cm. The anodes, which were of different dimensions, consisted of commercially pure aluminium, 1·2 mm. in thickness, which was cut accurately to give surfaces ranging from 1 cm.² to 50 cm.² according to the current densities under investigation. Before immersion in the bath the test-pieces were carefully

polished and cleaned.   Below the anodes the electrolyte was
vigorously stirred.

Figs. 30 and 31 show the variations in voltage necessary to
maintain the current density constant, as a function of time.   The
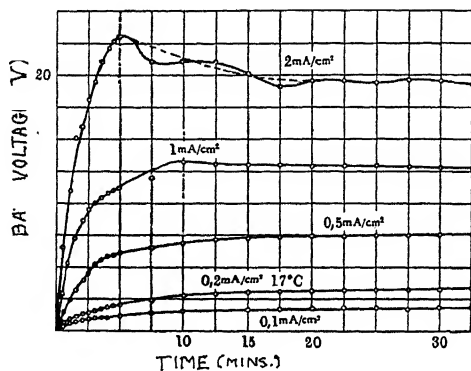course of the voltage curves which correspond to the current densities
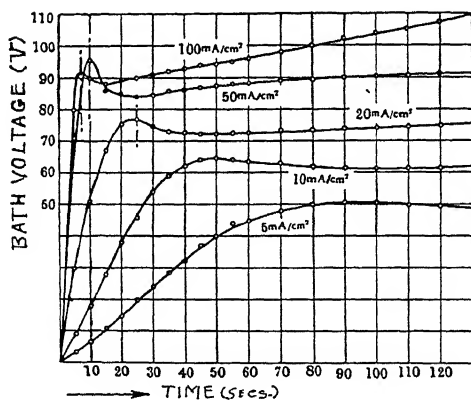

FIG. 30.

FIG. 31.

FIGS. 30 and 31.—Voltage/Time Curves at Constant Current Densities.

in excess of 2 ma./cm². resembles that of the curves in Fig. 23.[1]
The higher the current density the more rapidly does the voltage
attain its maximum value, and the shorter is the time which elapses
between the maximum and the minimum values.   The maximum
value (the critical voltage) can be measured quite accurately once
the current density exceeds a certain value.   The relationship

[1] See p. 93.

between the time required to attain the critical voltage and the current density is worthy of attention, since the product of this time and the current density is, as is shown in Table XX, approximately constant. This means that the quantity of electricity

TABLE XX.—RELATION BETWEEN TIME TAKEN TO ATTAIN THE CRITICAL VOLTAGE AND THE CURRENT DENSITY DURING OXIDATION AT CONSTANT CURRENT DENSITY.

Current Density, ma./cm².	Time to attain Critical Voltage, secs.	Quantity of Electricity, coulombs/cm².
0·1	—	—
0·2	—	—
0·5	—	—
1·0	600	0·6
2·0	300	0·6
5·0	100	0·5
10·0	50	0·5
20·0	25	0·5
50·0	10	0·5
100·0	7	0·7
200·0	4	0·8

which flows through the anode until the condition of the film corresponding to the onset of the critical voltage is reached is approximately constant.
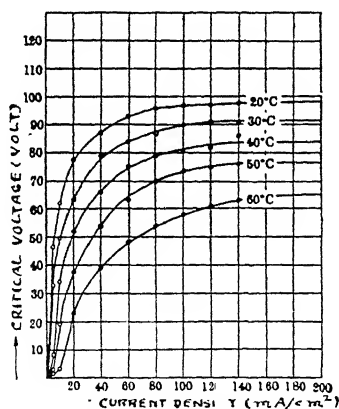

FIG. 32.—Influence of Temperature of Electrolyte on the Critical Voltage.

The influence which the temperature has on the critical voltage is apparent from Fig. 32. The higher the temperature (for constant current density) the lower is the critical voltage.

Figs. 33 and 34 show the influence of the concentration of the electrolyte on the critical voltage at room temperature (18° to 19° C.) for oxalic acid solutions. From Fig. 33 it may be seen that
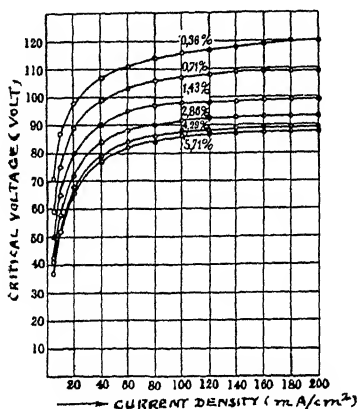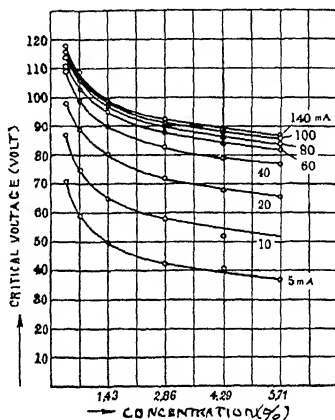

FIG. 33.   FIG. 34.

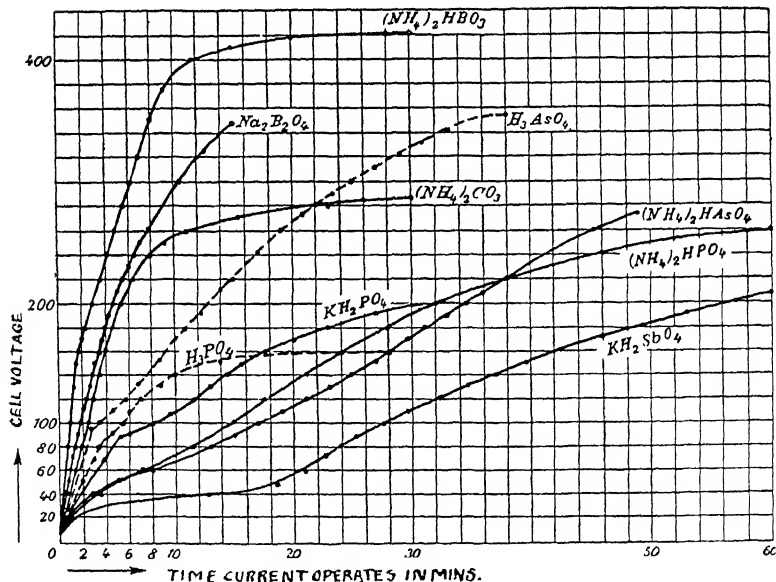FIGS. 33 and 34.—Influence of Concentration of Electrolyte on the Critical Voltage.

FIG. 35.—Development of the Anodic Voltage Loss of Aluminium with Time at a Constant Current Density of 0·005 amp./cm.² in Different Electrolytes. Temperature 0° C.[1]

[1] According to A. Güntherschulze.

the critical voltage rises as the concentration falls, and from Fig. 34 it is apparent that an increase in current density causes an increase in the critical voltage.

In Figs. 35 and 36 is shown the course of the voltage at a constant current density of 0·005 amp./cm.[2] during the forming of aluminium in a series of other electrolytes.[1] The beginning of spark discharge is in general the more distinct the sharper the bend of the curve. In the case of phosphoric acid there is no spark discharge at all, but only a diffuse glow discharge, which is uniformly distributed over the whole electrode. The maximum voltage is attained more rapidly with acids than with the corresponding salts. The curves, in the case of the salts, lie higher, since their solvent action is less than that of the acids. The curves for phosphoric acid (H_3PO_4) and arsenic acid (H_3AsO_4) and, to some extent, the curves for the salts of these acids show a peculiar break at about 85 v. In the case
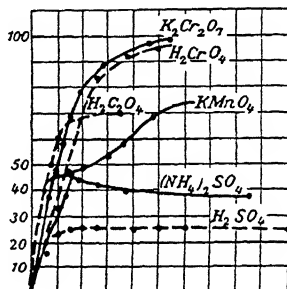

FIG. 36.—Anodic Voltage Loss of Aluminium with Time at a Constant Current Density of 0·005 amp./cm.[2] in Various Electrolytes. Temperature 0° C. Curves for acids are dotted ; those for the salt solutions are continuous.

of potassium permanganate ($KMnO_4$) the break occurs at 45 v. The dependence of the maximum voltage on the nature of the electrolyte may further be seen from the following figures, which were attained after 24 hours' forming in decinormal solutions :

	Volts			Volts
Na_2SO_4	40	$(NH_4)_2CrO_4$	.	. 275
Na_2SiO_3	445	$Na_2B_4O_7$	.	. 480
$KMnO_4$	112	NH_4HCO_3	.	. 425
$(NH_4)_2HPO_4$	470	Citric acid	.	. 536

Fig. 37 indicates the influence of the current density on the maximum voltage. The curves were obtained with ammonium borate solutions. The curves shown by continuous lines refer to the rise in voltage as a function of time, and the dotted curves show

[1] Curves according to A. Güntherschulze.

the increase in voltage in relation to the quantity of electricity passed. Whilst the final voltage is more rapidly attained with high current densities than with low current densities, the actual magnitude of the final voltage attained is practically independent of the current density so long as this does not fall below 0·002 to 0·001 amp./cm.² This lower limit of current density varies with the nature of the electrolyte. The dotted curves, which represent the effect of the quantity of electricity, show that there is no definite relationship between this quantity and the voltage. On the other hand, there is
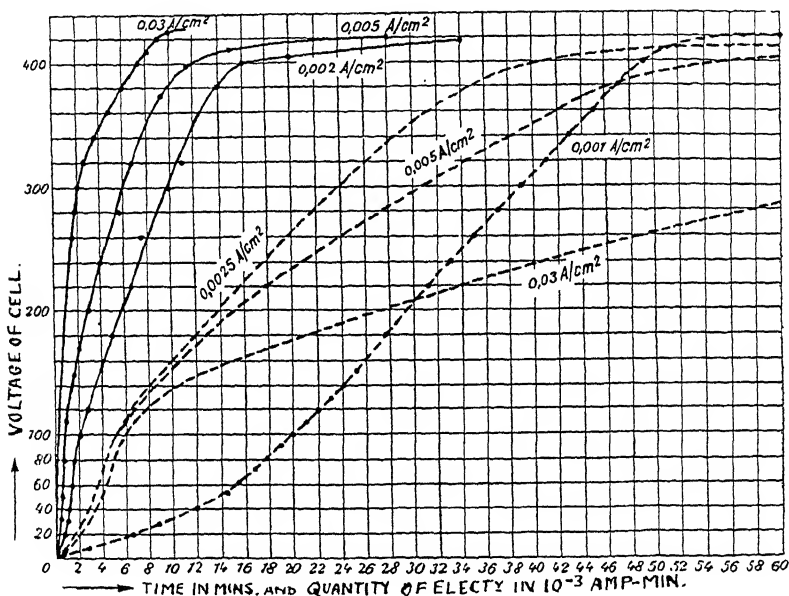

Fig. 37.—Development of Voltage with Time (——) and with Quantity of Electricity (- - - -) for Various Constant Current Densities in Ammonium Borate Solution.

an optimum range of current density (0·0025 to 0·005 amp./cm.²) in which the attainment of the voltage requires a minimum quantity of electricity.

Minimum Voltage

A. Güntherschulze has shown that a formed rectifier electrode does not allow any current to flow through below a certain voltage, the *minimum voltage*, even in the normal or forward direction. An aluminium anode formed at 300° C. in molten sodium nitrate up to 62 v., using direct current, was immersed in an electrolyte opposite a platinum electrode, and an oscillogram was taken to

show the course of the current and of the voltage after A.C. was applied.

The oscillogram is shown in Fig. 38.[1] It can be seen that the current first begins to flow in the forward direction when the voltage on the cell has risen to a point *a*, which represents the minimum voltage. From *a* onwards, the voltage is almost constant, that is
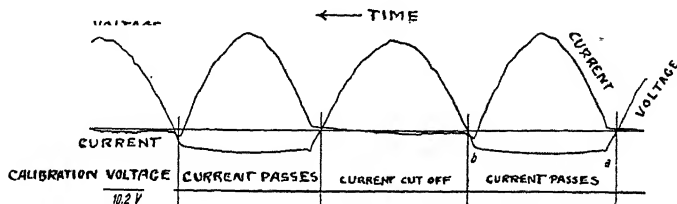

FIG. 38.—Oscillogram showing the Minimum Voltage in the Forward Direction.

to say, it is independent of the current, up to the point *b*, at which the current again becomes zero.

O. Mohr has investigated the relationship between the minimum voltage and the forming current density, the forming voltage, and the nature of the electrolyte, with particular reference to concentra-
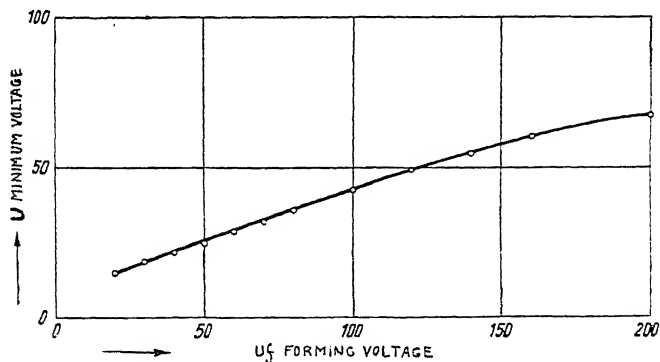

FIG. 39.—Minimum Voltage in relation to the Forming Voltage.

tion, anion, cation and temperature (among other factors), for tantalum and aluminium.

He found that the minimum voltage is little affected by the forming current density. As the forming voltage increases the minimum voltage rises almost linearly. Fig. 39 shows the course of the minimum voltage $U_{min.}$ in relation to the forming voltage U_1 for aluminium. The curvature which is exhibited beyond about

[1] According to A. Güntherschulze.

120 v. is attributable to disturbances due to the beginning of dissolution of the film as a consequence of the rise of temperature at the anode. The measurements were carried out in solutions of ammonium citrate, ammonium carbonate and ammonium borate. Difficulties were experienced with other electrolytes because of the solubility of the oxide film.

The nature of the anion and of the cation of the electrolyte has little or no influence on the phenomena in the forward direction so long as there is no metallic deposition, *i.e.* so long as there are no heavy metal cations in the electrolyte. The cations Na· and K· occupy a special position because of the fact that they certainly induce changes in the film itself. The influence of the concentration
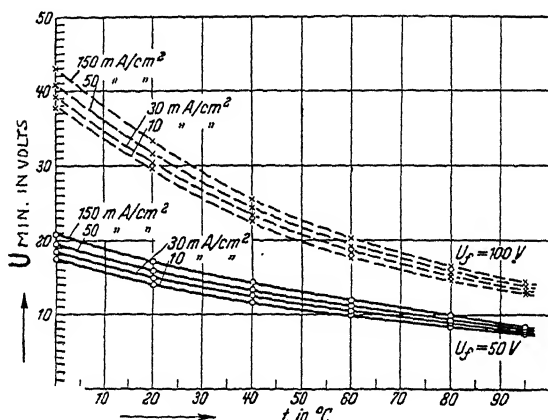

Fig. 40.—Falling off of the Minimum Voltage as the Temperature of the Electrolyte rises.[1]

of the electrolyte on the minimum voltage is small. On the other hand, the minimum voltage is to a large extent dependent on temperature. Over the range 0° to 96° C. the minimum voltage falls off in different electrolytes in precisely the same way, so that this variation may be regarded as independent of the nature of the electrolyte. Fig. 40 shows how the minimum voltage falls off as the temperature of the electrolyte rises, the electrode being tantalum which had been formed at 50 and 100 v. respectively ($U_f = 50$ and 100 v.). The electrolyte used for the determinations was decinormal ammonium nitrate solution. The variation with temperature of the minimum voltage is exactly similar in the case of tantalum and aluminium. The frequency of the applied alternating voltage has no effect on the minimum voltage.

[1] According to O. Mohr.

B.—Alternating Current Treatment

Oxide films may also be produced by using A.C. Where an alternating voltage is applied to the aluminium cell (*cf.* Fig. 41) the film can form only during the half-period in which the aluminium is anode. In the second half-period, hydrogen is evolved at the aluminium. It is obvious that for this reason alone the oxidizing effect of a symmetrical alternating current of given effective voltage can, at most, equal half that of a direct current of the same voltage in the same time. During formation of the film the resistance in the rectifying direction increases, and in consequence the current density in the same direction decreases. A direct current component $I_{D.C.}$ is superimposed on the A.C., and the ratio $I_{D.C.} : I_{eff.}$, in which $I_{ff.}$ is the effective value of the current passing through, is a measure
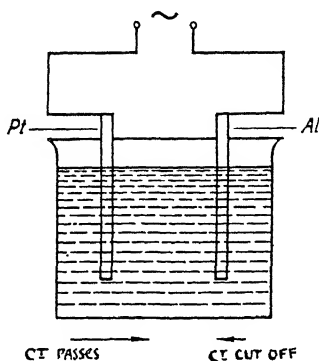

FIG. 41.—Diagram showing the Behaviour of the Current when an Alternating Voltage is applied to an Aluminium Cell. The difference in the currents in the two directions is shown by the lengths of the arrows.

of the valve effect. This ratio approaches a constant value as forming progresses, the constant value representing the end state. According to J. Zenneck, this value is independent of the previous history of the cell. Accordingly, it becomes smaller during forming if, as a consequence of a previous forming by D.C. or a heavier A.C., it has been greater than would correspond to the end state of the subsequent forming current. As in the case of D.C. treatment, the end state in this case, also, is not completely constant. The ratio $I_{D.C.} : I_{eff.}$ still varies slightly, if slowly, when the treatment is prolonged. The D.C. component $I_{D.C.}$ was controlled by means of a hydrogen voltameter.

According to E. Wilson, forming proceeds more rapidly the smaller the surface of the electrode, the voltage and frequency being fixed ; the current density is, therefore, of prime importance.

Figs. 42 and 43 show two oscillograms which were obtained by J. Zenneck. The forming was carried out on two initially unformed aluminium surfaces of different magnitudes, using approximately

FIG. 42.
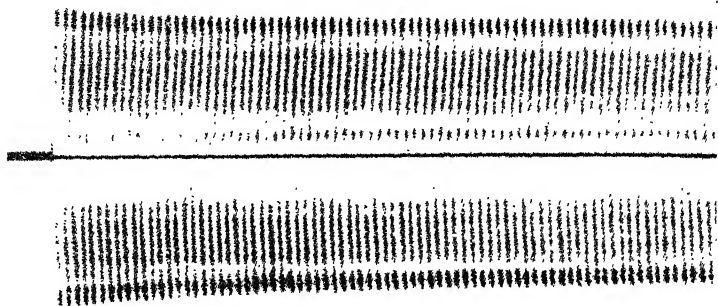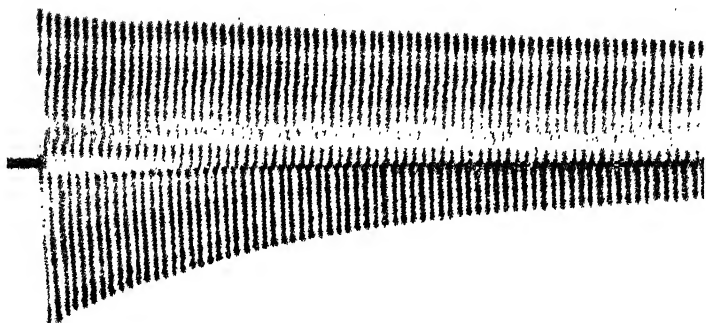

FIG. 43.

FIGS. 42 and 43.—Oscillograms showing the Influence of the Current Density on the Rate of Forming with A.C.

equal currents ($I_{\text{eff.}}$ = approx. 4 amp.) with A.C. of 50 cycles. When Fig. 42 was taken the surface was about 100 cm.², and in the case of Fig. 43 it was about 3·1 cm². In both cases the exposure period was 1·5 sec. In the oscillogram shown in Fig. 42 inequality

of amplitude is only just detectable, whilst in Fig. 43 the forming
is already further advanced.   With a surface of 500 cm.² no inequality
of amplitude at all could be observed.   The current density is of
fundamental importance in the end state as well; the higher it is
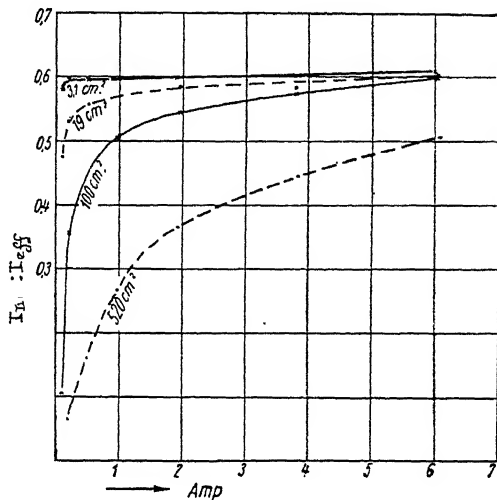
FIG. 44.—The Ratio of $I_{D.C.}$: $I_{eff.}$ in relation to the Current Density.

for a given voltage the greater is the value of the ratio $I_{D.C.}/I_{eff.}$,
it being immaterial whether any resistance in the circuit external
to the cell is ohmic or inductive in character.

Where the resistance is ohmic the conditions are readily apparent.
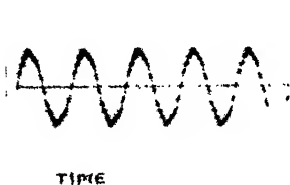
FIG. 45.   FIG. 46.

FIGS. 45 and 46.—Oscillograms showing the Unsymmetrical Course of an Alternating
Current during the Forming of an Aluminium Electrode.

Fig. 44 shows the results of a series of measurements carried out
with a transformer voltage of about 100.   The figures marked on
the curves represent the surface area of the aluminium electrodes
employed.   As the surface decreases the current density increases
and, accordingly, so does the ratio $I_{D.C.}/I_{eff.}$ Fig. 45 shows the

oscillogram[1] derived for the cell with 520 cm.[2] aluminium surface, where some lack of symmetry is already apparent ; whilst the valve effect of the cell with 3·1 cm.[2] aluminium surface is almost complete, as is shown by the oscillogram[1] in Fig. 46.

The rôle of the current density is, therefore, the same in alternating current forming as it is in direct current oxidation. In both cases the velocity of forming increases as the current density increases.

In order to produce films of sufficient thickness for protective purposes the production of a rapid and complete valve action should be avoided. The objective is best attained by using an electrolyte in which the aluminium or the oxide film exhibits a certain, if slight, solubility. On the other hand, where it is intended to use the aluminium for rectifiers or condensers, electrolytes should be selected in which the aluminium exhibits the minimum solubility and the maximum rectifying effect. For condensers, the aim is to produce extremely thin films of high rectifying efficiency with the object of attaining large capacities.

There is no chemical action on the oxide film by the hydrogen which is liberated at the aluminium during passage of the current in the forward direction.[2] As we have already seen from the high heat of formation,[3] more energetic means are required for the reduction of aluminium oxide. Any effect of the hydrogen, which is supported by the uncombined oxygen in the reverse direction, must be exclusively mechanical. The gases liberated when the direction of the current is rapidly alternated bring about a rapid exchange of the electrolyte in the pores, and this results in the fact that from the commencement of forming the pores are more numerous than would occur with direct current operation ; and because of the solvent effect of the frequently renewed electrolyte these pores become widened. The appreciably lower hardness and the flexibility of A.C. films as compared with those produced by D.C. point to the structure being loose and spongy, and the explanation for this is to be found in the above facts.

The thickness of A.C. films is far less than that of the corresponding D.C. films, since the ratio of the forming period to the dissolution period is 1 : 2, whilst with D.C. forming this ratio is 1 : 1. The conditions governing the attainment of equilibrium between growth and dissolution of the film are, therefore, shifted in favour of dissolution when A.C. treatment is used.

In the case of A.C. treatment, there exists the possibility of simultaneous oxidation of two aluminium electrodes connected to the two poles of the current source, an arrangement which is made use of in electrolytic condensers and is frequently applied also in the commercial production of protective films. The advantage of this method of operation consists in a better utilization of the bath,

since it permits of the treatment of two or more objects in pairs, and since the cathodes can be dispensed with. The quality of the films on objects oxidized in pairs by bipolar treatment does not differ appreciably provided the bath is arranged to operate with the most uniform load possible at both electrodes. In this connection the magnitude of the surface is as important as the chemical composition of the objects to be oxidized at the two electrodes. It is, therefore, not feasible to have a very large aluminium surface at one electrode and a very small aluminium surface at the other, nor is it possible to have pure aluminium at one pole and duralumin at the other, since either would cause great asymmetry of the A.C. If, however, the current densities, and hence the rates of forming, are different at the two sides of the bath, the consequence is an unequal film formation on the objects connected to the two poles.

Different Arrangements for A.C. Treatment
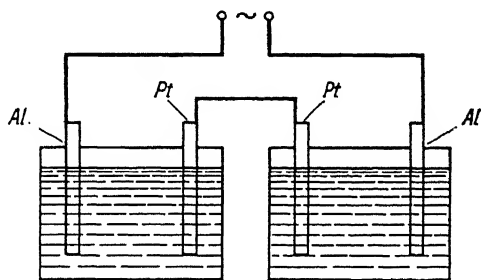
FIG. 47.—Double Cell Arrangement for A.C. Treatment.

It is possible to overcome the above difficulties in two ways, either by preforming one electrode, or else by working with two baths. In the first case, the already formed electrode behaves as a valve : it blocks the passage of the current during the half-period in which it is the anode, and allows it to pass unhindered in the second half-period, in which it is the cathode, so that effectively the unformed electrode behaves only as anode. Such an arrangement, therefore, approximates closely to an interrupted D.C. anodic treatment, and it is employed only in those cases where special effects are desired. It has the disadvantage that the preformed electrode undergoes a change during the operation of the bath, so that this method is, to some extent, unreliable. Another difficulty which is presented is the unsymmetrical use of the A.C., which is uneconomic. Accordingly, the use of a preformed electrode in A.C. oxidation would be of interest only if the films produced possessed technical advantages which could not be achieved otherwise.

The second possibility, which was proposed by A. Güntherschulze,

8

appears much more desirable. In this arrangement the difficulties which arise in A.C. treatment are circumvented by using two separate cells.

The arrangement shown in Fig. 47 is self-explanatory. In place of the metallically conducting platinum electrodes, other unattackable materials, such as graphite, may be used. The aluminium electrodes may also be replaced by other valve metals, and the electrolytes in the two cells may be different. With this arrangement it is possible to a large extent to control the ratio of the currents in the two directions and, hence, to control the film formation. The sole disadvantage with this arrangement is the extra space required for the accommodation of two cells.

Influence of Frequency
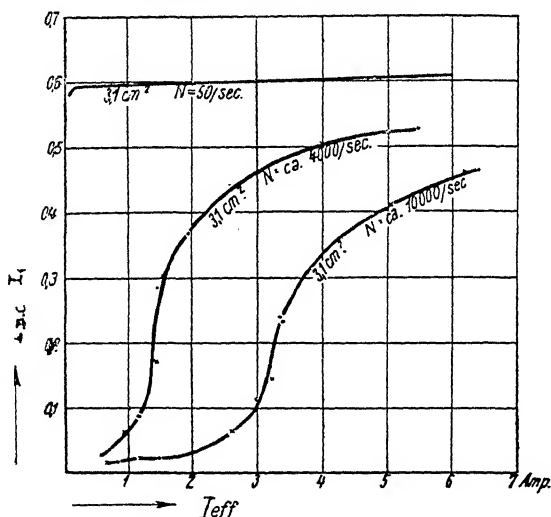
FIG. 48.—Curves showing how Valve Action becomes less Effective as Frequency increases.

J. Zenneck[1] extended his investigations on the influence of the C.D. to high-frequency currents. As would be expected from the experiments discussed above, he discovered in the first place that with an A.C. of 4,000 hertz the value of the ratio $I_{D.C.}/I_{eff.}$ for a cell with 10 cm.[2] aluminium surface was far below that of a cell with 3·1 cm.[2] aluminium surface : that is to say, the rate of forming increases as the C.D. increases, with high-frequency currents as well. Further researches showed, as Fig. 48 indicates, that a definite valve effect can be obtained even with frequencies as high as 4,000 and 10,000 hertz ; but the effect diminishes as the frequency

[1] See p. 109.

increases. J. Zenneck's researches were carried out with an ohmic external resistance.

Combined D.C. and A.C. Treatment

The combination of D.C. and A.C. for the purpose of the oxidation of aluminium can be carried out in different ways. We have already referred to one possibility of applying an A.C. to an aluminium cell ; and we have seen that the rectifier effect in this case is equivalent to a super-imposition of a D.C. component on the A.C. With this arrangement it is not possible to arrive at complete rectification, where the current curve in the oscillogram rests exactly on the zero line (*cf.* Figs. 46 and 50), since the limiting value of complete valve action can never be attained with the current densities available in practice.

In order to transform A.C. completely into rectified A.C. or pulsating current, it is necessary to use an auxiliary external source of D.C. Working with rectified A.C. requires the use of a special circuit (Fig. 49). The A.C. is led through a transformer coil, *T*, which can be tapped at the centre, and through two anodes, *A*, to the electrolytic cell *Z*. The D.C. to be superimposed on the A.C. is led through the central tapping into the transformer coil and returned through the cathode, *K*, of the cell to the D.C. source *G*. Full rectification of the A.C. by the superimposed D.C. is attained when the pulsating current is posed exactly on the zero axis *N* (*cf.* Fig. 50).
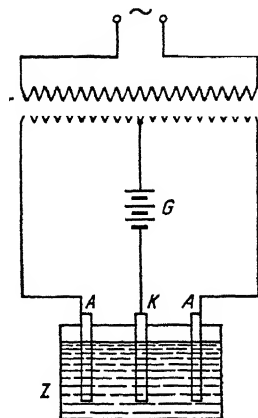
FIG. 49.—Diagram showing Arrangement for super-imposing A.C. on D.C.

FIG. 50.—Accurately Rectified A.C. (Pulsating Current).

This arrangement has been recommended in order to overcome the difficulties experienced during D.C. treatment in connection with pitting of the aluminium surface or burns which penetrate deep into the metal. With superimposed A.C. this risk is completely removed. The process has not been adopted in European countries because of the high cost of the plant and of operation, and also because the difficulty mentioned can be easily overcome by appropriate D.C. treatment without superimposition of A.C.

The third method of combining A.C. with D.C. consists in using the two types of current one after the other. This method of working is used in order to endow the comparatively soft A.C. films with increased mechanical resistance by subsequent treatment with D.C.[1] In this way the harder D.C. film is formed underneath the A.C. film. This process has proved useful for certain special purposes.

Characteristics

A curve which shows the relationship between the voltage and the current density (C.D.) is known as a *characteristic*. According as to whether the curve applies to D.C. or to A.C. it is called a *static* or a *dynamic* characteristic.
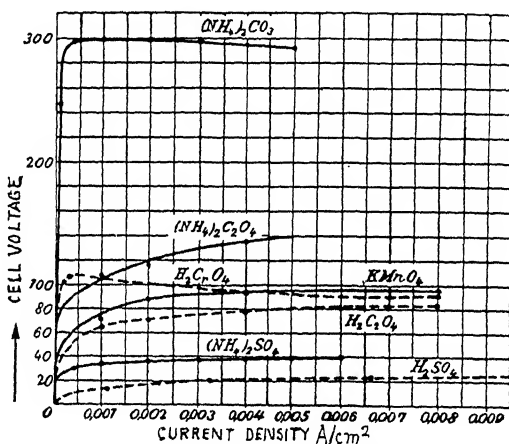
FIG. 51.—Static Characteristics of the Aluminium Anode in Different Electrolytes.

A. Güntherschulze has investigated the relationship between the C.D. and the voltage in the aluminium cell for a number of different electrolytes by employing a series of different C.D.s and recording the corresponding voltages. He carried out measurements both for increasing and decreasing C.D.s and took the average of the two results, which, in general, varied by only a few volts. In the case of some electrolytes the voltage was reached almost immediately, but in other electrolytes an approximately constant value was attained only after a lag of about a minute.

Fig. 51 shows the static characteristic [2] of aluminium for some electrolytes in commercial use, such as chromic acid (H_2CrO_4), oxalic acid ($H_2C_2O_4$), and sulphuric acid (H_2SO_4). The voltages corresponding to given current densities fall off in these electrolytes

[1] *Cf.* Fig. 81, p. 141. [2] According to A. Güntherschulze.

in the above order, owing partly to the increase in thickness, and partly to the porosity, of the films in question. The steep rise of the voltage in ammonium carbonate solution, $(NH_4)_2CO_3$, is characteristic of the very marked valve effect in this electrolyte, in which the aluminium oxide is practically insoluble.

Fig. 52 shows the influence of the concentration on the course of the static characteristic for aluminium in ammonium borate and ammonium carbonate solutions of different concentrations.[1] As the concentration falls off, the maximum voltage and the steepness
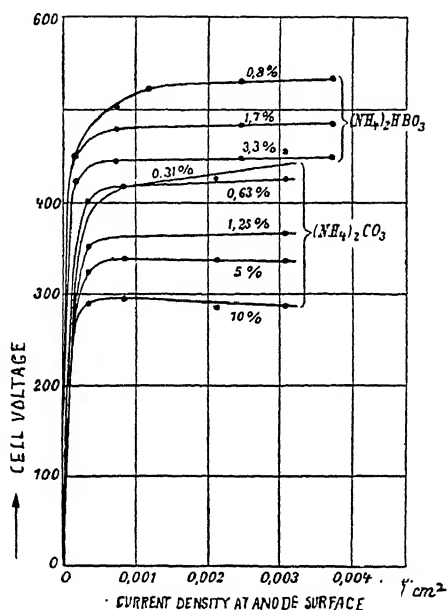
FIG. 52.—Static Characteristics of the Aluminium Anode for Different Electrolyte Concentrations. Temperature $0°$ C.

of the curves increase, in consequence of the improved rectifying effect.

The next diagram (Fig. 53)[1] shows the influence of the temperature on the static characteristic for tantalum in 0·02 per cent. potassium carbonate solution, and for aluminium in 1·7 per cent. ammonium borate solution. The curves indicate that a rise in temperature (i) lessens the steepness of the rise in voltage as the C.D. is increased; and (ii) increases the C.D. at which the maximum voltage is attained.

It should be noted that aluminium is much more greatly affected by the temperature in all other electrolytes than ammonium borate solutions, so that the voltages attained in this case represent

[1] According to A. Güntherschulze.

exceptionally high values. The leakage current (that is to say, the current which remains when a given voltage, smaller than the maximum, is attained) is much greater at high temperatures in the case of aluminium than in the case of tantalum. It is not intended in this book to go very thoroughly into the complicated relationships appertaining to the dynamic characteristic. They have been exhaustively discussed in various other works.
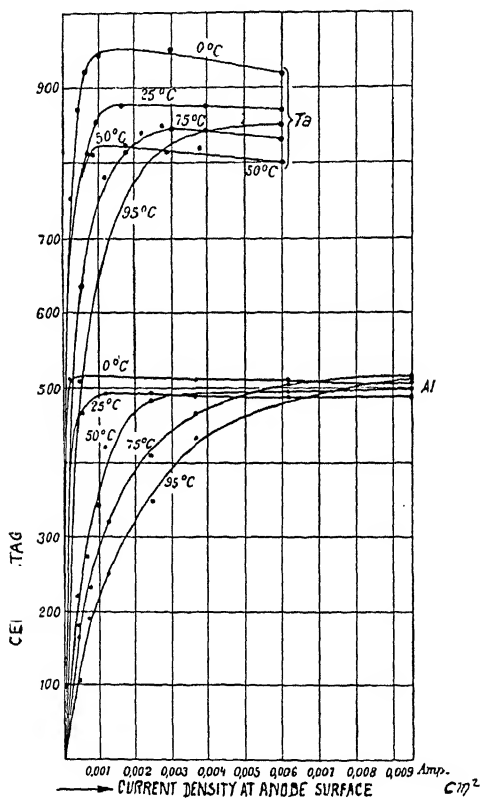
FIG. 53.—Static Characteristics of Aluminium and Tantalum Anodes at Different Temperatures.

Bairstow and Mercer determined the variation of the C.D. with increasing and decreasing alternating voltage for different electrolytes. They used electrodes of lead and of aluminium. Several tests were carried out at different temperatures with each electrolyte, the temperature being maintained constant throughout each test. The voltage was regulated by means of a rheostat, and after each change of voltage the current was not read off until it had attained

an approximately constant value. In the case of low voltages, as much as 2 to $2\frac{1}{2}$ hours were necessary in some cases, but the times were correspondingly shorter for higher voltages, at which the C.D. rapidly attained its maximum value.
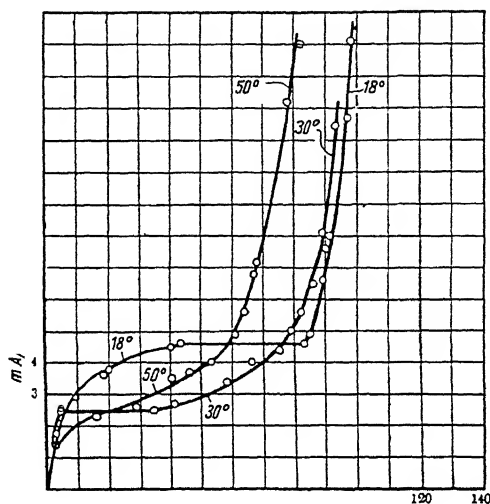
FIG. 54.—Current Density/Voltage Curves for an Ammonium Phosphate-Aluminium Cell using A.C.
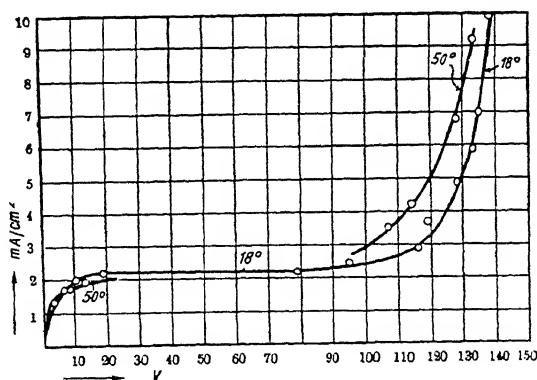
FIG. 55.—Current Density/Voltage Curves for an Ammonium Borate-Aluminium Cell using A.C.

Table XXI and Figs. 54 and 55 show the results obtained by these authors using diammonium phosphate at 18°, 30° and 50° C. respectively, and ammonium borate at 18° and 50° C.

TABLE XXI

Diammonium Phosphate

18° C.		30° C.		50° C.	
Voltage.	Current Density, ma./cm.²	Voltage.	Current Density, ma./cm.²	Voltage.	Current Density ma./cm.²
3	1·73	2·6	1·8	2·4	1·4
4·8	2·56	4·5	2·5	16	2·3
9·6	2·9	34·5	2·5	28·7	2·6
18·3	3·6	40·1	2·7	40·1	3·5
20	3·8	58	3·4	46	3·7
40·1	4·5	66	4·0	53	4·0
43·7	4·6	75	4·4	61	4·9
83	4·6	79	5·0 ·	64	5·6
85	4·9	82	5·6	67	6·8
89	6·6	86	6·5	68	7·2
90	7·6	89	8·1	69	8·2
91	8·0	93	11·5	78	12·2
96	11·7	96	15·6	82	14·0
98	14·1	99	21·0	83	16·9
102	17·2	—	—	85	22·4

Ammonium Borate

18° C.		50° C.	
Voltage.	Current Density, ma./cm.²	Voltage.	Current Density, ma./cm.²
3·8	1·35	8·55	1·72
6·8	1·7	13·2	1·92
10·2	1·97	—	—
19	2·2	107	3·5
79	2·2	114	4·2
95	2·46	128	6·8
116	2·88	133	9·2
119	3·67		
128	4·84		
133	5·85		
135	6·95		
138	9·9		

Falling Voltage.			
131	4·9		
128	4·6		
124	3·5		
118	2·6		
110	2·25		
100	1·65		
89	1·5		
66	0·58		

(a) Direct Current Treatment

Theoretical Increase in Weight of the Aluminium

ERRATUM.

On p. 121, after first paragraph, insert:

C.—Growth of Oxide Film during D.C. or A.C. Treatment

The growth of the oxide film is a function of the C.D. and of the solution velocity, which increase with temperature, and also depend on the applied voltage, type of current, and nature and concentration of the electrolyte. The composition of the basis metal is also of great influence. From the large number of variables arise many possibilities of influencing the growth and the properties of the films.

The interesting part of these curves is that where the current density remains constant for a considerable time in spite of increasing voltage. In a number of experiments this constancy was maintained for several hours, until the current, on a further slight increase in the voltage, suddenly rose to high values (*cf.* the curve obtained at 18° C., Fig. 54). G. E. Bairstow and R. Mercer explain the constancy of the current density by an increase in the resistance of the film in the corresponding voltage range, while they ascribe the sudden rise in current to a decrease in the capacity of the film.

(a) Direct Current Treatment

Theoretical Increase in Weight of the Aluminium

If the whole of the oxygen liberated by the current were used in the formation of the oxide film, and if no dissolution by the
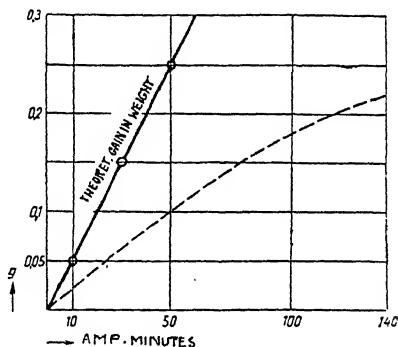
FIG. 56.—Gain in Weight of the Aluminium Anode in relation to the Quantity of Electricity passing.

electrolyte of the film, once formed, took place, the increase in weight of the aluminium anode would be directly proportional to the quantity of electricity passing through it. In accordance with Faraday's law, therefore, the increase in weight ΔG per ampère-minute would be :

$$\Delta G = \frac{8}{26 \cdot 8 \times 60} = 0 \cdot 00497 \text{ gram.}[1]$$

Fig. 56 shows the straight line corresponding to the theoretical increase in weight in relation to the quantity of electricity. In electrolytes which have a solvent effect the increase in weight is actually considerably smaller, and is indicated in the diagram by the dotted curve. In addition to the influence of the solvent action,

[1] Equivalent weight of oxygen = 8 ; 26·8 ampère-hours are necessary to separate 1 gram-equivalent.

the fact that some 4 to 5 per cent. of the oxygen discharged at the anode remains uncombined also affects the results. According to Meserve, who used a sodium bicarbonate solution for his investigations, only 96 per cent. of the oxygen discharged at the anode takes part in the reaction, whilst other authors give a value of 95 per cent. for oxalic acid. In both cases, therefore, there is an excess of oxygen, and this oxygen is initially in the extremely active atomic form, so that direct combination occurs with the reactive aluminium.

Increase in Weight in Relation to the Quantity of Electricity at Different Voltages
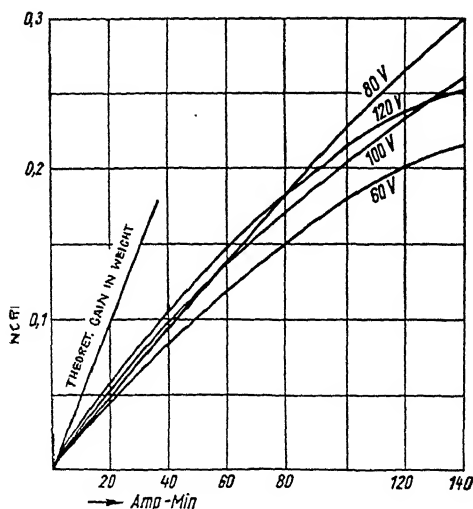
FIG. 57.—Variation in Weight of the Aluminium Anode at Different Voltages in relation to the Quantity of Electricity. Aluminium surface = 5 cm.^{2}; 1·43 per cent. oxalic acid; 10–17° C.; D.C.

Fig. 57 indicates the influence of the voltage on the relationship between the increase in weight and the quantity of electricity. The curves were derived from the oxidation of aluminium in 1·43 per cent. solutions of oxalic acid at 10° to 17° C., and they show that the most favourable voltage in this electrolyte is about 80. At 60 v. the C.D. is still too small, so that the growth requires too much time to produce the desired film thickness. At 100 v. and 120 v. the C.D. is too high ; too much unused oxygen is lost, and in consequence of the heating effect the film is redissolved to too great an extent.

Simultaneous Variation in Thickness of the Aluminium and of the Film

The decrease in thickness of an aluminium sheet, and the increase in thickness of the film, during oxidation in 1·43 per cent. oxalic acid solution are shown in Figs. 58 and 59 as a function of the
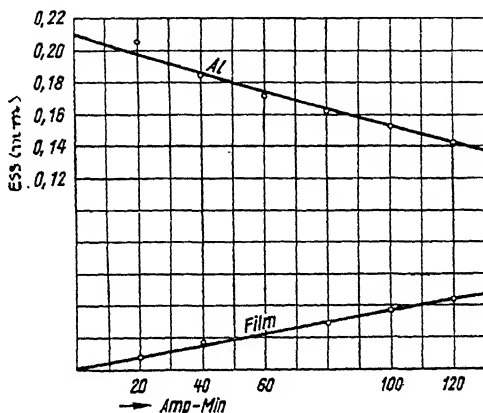
FIG. 58.—Variation in Thickness of the Aluminium and the Film in relation to the Quantity of Electricity. 18°–20° C.; 0·02 amp./cm.²; D.C.
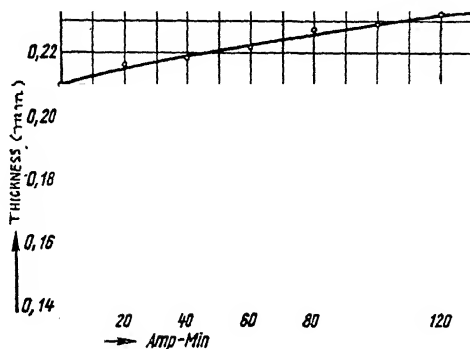
FIG. 59.—Total Increase in Thickness of an Aluminium Sheet in relation to the Quantity of Electricity. 18°–20° C.; 0·02 amp./cm.²; D.C.

quantity of electricity. Fig. 59 shows the total increase in thickness. The C.D. during the tests was 0·02 amp./cm.² The total thickness increases approximately linearly with the quantity of electricity, but at the same time the curve indicates, in the gradual flattening which occurs, the solvent effect which the oxalic acid has on the aluminium. In contradistinction to this, the course of the curve

representing the increase in thickness of the film remains linear throughout if no account is taken of the variation in thickness of the aluminium, as can be seen from Fig. 58. It is of interest also to compare Fig. 29.[1]
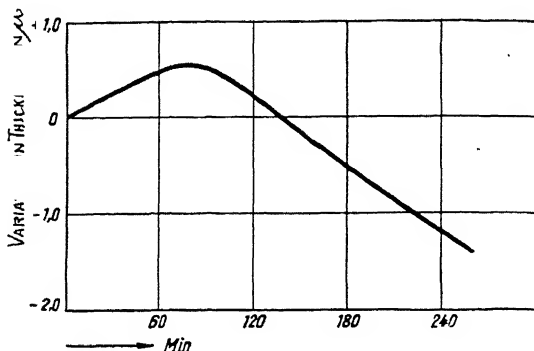
FIG. 60.—Variation in the Total Thickness of an Aluminium Sheet as Oxidation Progresses.

S. Wernick has observed the variation in total thickness of an aluminium sheet as oxidation progresses, in moderately dilute sulphuric acid, by direct measurement with a micrometer gauge. The variations which he found are shown in Fig. 60 as a function of time. It can be seen from this figure that the total thickness

ORIGINAL ALUMINIUM SURFACE

FILM SURFACE IN EACH PHASE

FILM

BASIS METAL (Al)

ALUMINIUM SURFACE IN EACH PHASE
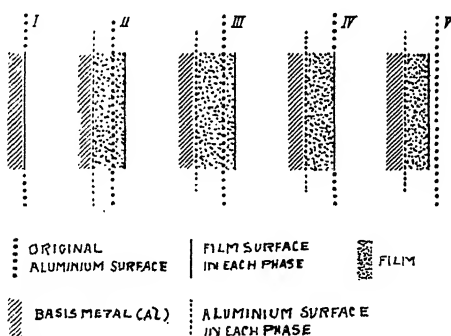
FIG. 61.—Diagrammatic Representation of the Variation in Thickness of an Aluminium Sheet during Oxidation.

initially undergoes an increase, which reaches a maximum of 0·5 μ after about 75 minutes, after which the total thickness decreases again as time goes on. After some 140 minutes the original thickness of the sheet is re-attained. From this point the total thickness steadily falls off.

[1] P. 101.

Fig. 61 indicates the individual phases of the film formation. At a given stage (IV) the total change in thickness is zero. As the treatment is continued (V), the film thickness falls off to a point where the total thickness is less than the original thickness of the aluminium. In the commercial processes of oxidation the surface of the aluminium is not worn away to such an extent, since the conditions of oxidation, with regard for technical and economic requirements, are closely controlled. In general every precaution should be taken to prevent any decrease in the total thickness below
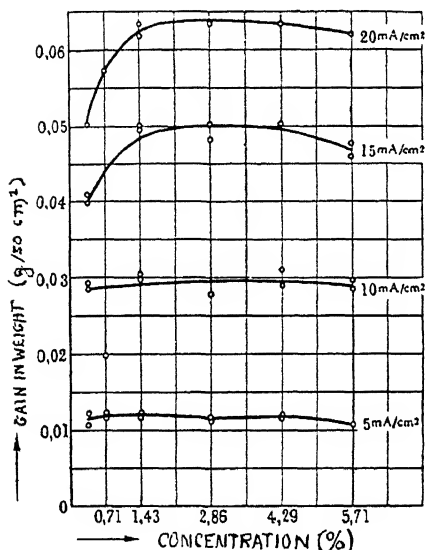
Fig. 62.—Gain in Weight of Aluminium at Constant C.D.'s in relation to the Concentration of the Oxalic Acid, D.C.
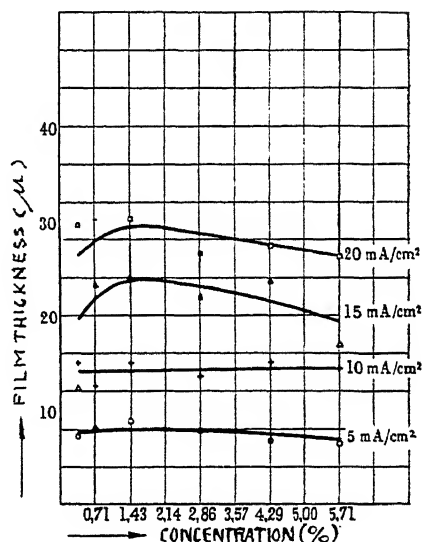
Fig. 63.—Growth in Thickness of the Film at Constant C.D.'s in relation to the Concentration of the Oxalic Acid, D.C.

the original thickness of the aluminium, as this would represent a useless waste of current and a weakening of the material.

The increase in weight, the increase in thickness of the film and the decrease in thickness of an aluminium sheet for different constant current densities and different concentrations of oxalic acid are shown in Figs. 62 to 64. With small current densities the concentration does not exert any influence on the growth. At high current densities the increase in weight in dilute solutions is small; it increases rapidly up to a concentration of about 2 per cent. Approximately the same tendency is observed with the increase in thickness of the film and the decrease in thickness of the aluminium : at high current densities in dilute solution, the temperature of the electrolyte in the neighbourhood of the electrode rises, as a

consequence of the large energy consumption at the anode, and the film formed has a tendency to dissolve. In such cases the increase in weight and the thickness of the film are, naturally, small. It is hardly necessary to point out that in the more concentrated solutions the tendency of the film to dissolve increases. Fig. 64 shows the theoretical values for the decrease in thickness of the aluminium as dotted lines. The curve corresponding to the high C.D. of 20 ma./cm.^{2} lies appreciably below the theoretical line for the same C.D., which points to a strong attack of the aluminium
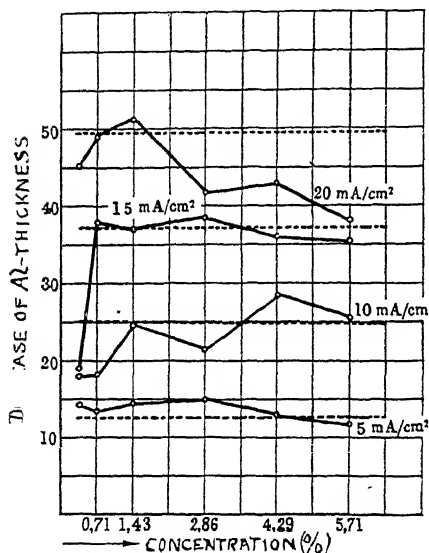
FIG. 64.—Decrease in Thickness of the Aluminium at Constant C.D.'s in relation to the Concentration of the Oxalic Acid, D.C.
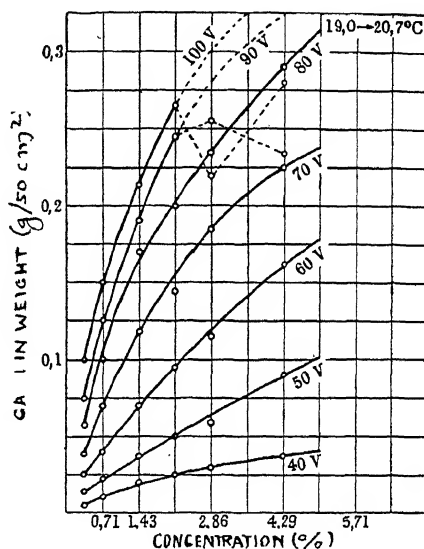
FIG. 65.—Gain in Weight of Aluminium at Constant Voltages and Different Concentrations of Oxalic Acid, D.C.

by the oxalic acid, and a considerable liberation of oxygen, which does not take part in the oxidation process.

The variations in weight and in the thickness of the film, and the decrease in thickness of the aluminium, are shown in Figs. 65 to 67 for different constant voltages of 40, 50, 60, 70, 80, 90 and 100, and for different oxalic acid concentrations. In view of the difficulties presented by the maintenance of a constant temperature of the electrolyte during the tests, the values obtained at the high voltages show considerable deviations. In spite of this fact, the curves give a fairly true picture of the actual conditions, the weight of the test-piece and the thickness of the film increasing with voltage and concentration of the electrolyte, whilst the reverse is true of the thickness of the metal.
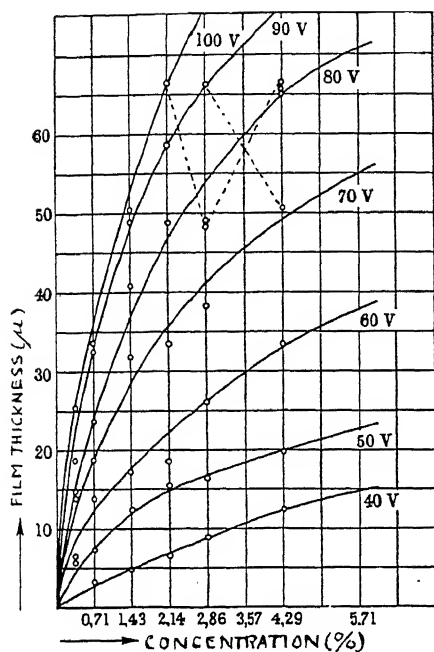
FIG. 66.—Growth of Film Thickness at Constant Voltages and Different Concentrations of Oxalic Acid, D.C.
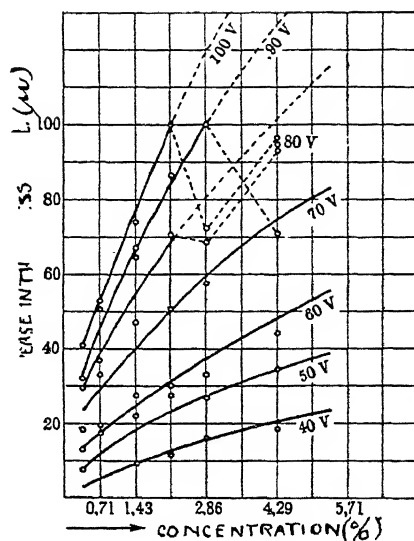
FIG. 67.—Decrease in Thickness of the Aluminium at Constant Voltages and Different Concentrations of Oxalic Acid, D.C.
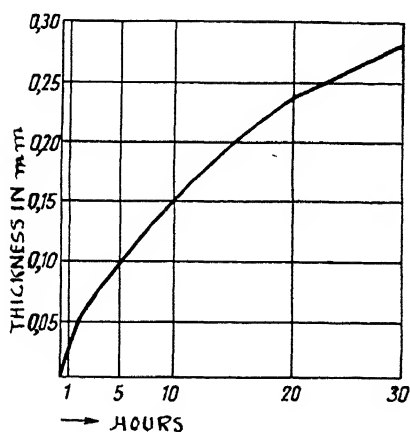
FIG. 68.—Growth in Thickness of Film with Time during a 30 Hours' Test Period, D.C.

Increase in Film Thickness with Time

In Fig. 68[1] the increase in thickness of the oxide film is shown as a function of the period of oxidation during a 30 hours' treatment of aluminium at 60 v. and 17° C. in 5 per cent. oxalic acid solution. The flattening of the curve indicates that the growth of the film with time lags behind the solvent effect of the oxalic acid.

In this example the film attains a thickness of more than 0·25 mm., from which it is clear that it is not difficult to oxidize almost right through an aluminium sheet of 0·5 mm. and over. As the oxidation progresses the thickness of the aluminium decreases,
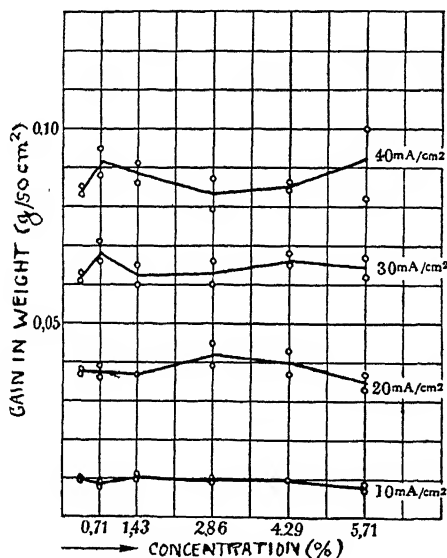
Fig. 69.—Gain in Weight of Aluminium in relation to the Concentration of Oxalic Acid (per cent.) for A.C. Treatment and Constant C.D.

until the cross-section is so small that the metal actually melts at the thin areas, in consequence of the increasing resistance. Ultimately the passage of the current is completely interrupted, with the result that in the interior of the oxide film there are always to be found more or less minute unoxidized fragments of aluminium.

(b) Alternating Current Treatment

Increase in Weight and Growth in Thickness of the Film : Decrease in Thickness of the Aluminium

Where A.C. is used, with two aluminium electrodes, the formation of the film is considerably slower than with D.C. oxidation. The

[1] According to researches by Messrs. Siemens & Halske A.-G.

increase in weight, the growth in thickness of the film, and the decrease in thickness of the aluminium for 50-cycle A.C. are shown in Figs. 69 to 71, the current density being constant at 10, 20, 30 and 40 ma./cm.^{2} respectively and the oxalic acid concentrations being as shown.

Since the film can grow only during the half-period in which the test-piece is the anode, double the C.D. was used ; in spite of this the values reached in the same time approximate only very
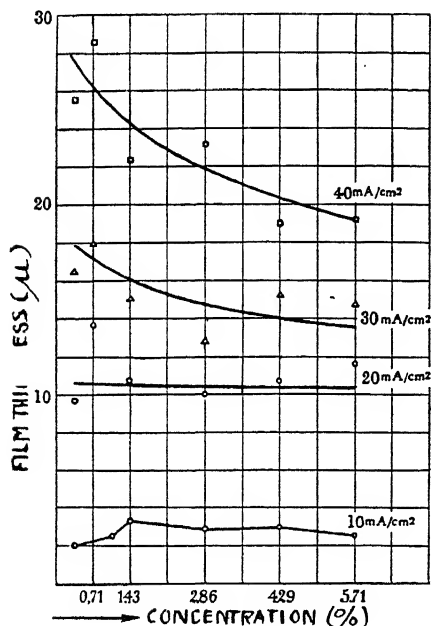
FIG. 70.—Growth in Thickness of Film in relation to the Concentration of Oxalic Acid (per cent.) for A.C. Treatment and Constant C.D.'s.
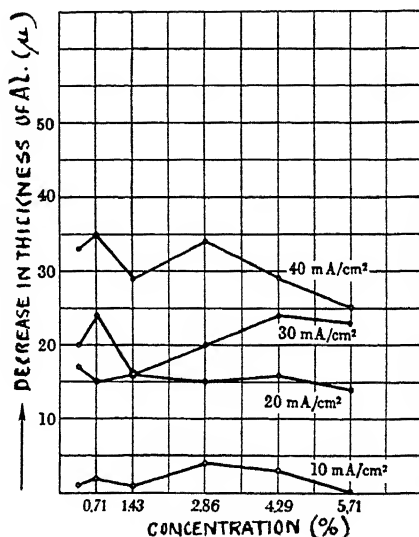
FIG. 71.—Decrease in Thickness of the Aluminium in relation to the Concentration of Oxalic Acid (per cent.) for A.C. Treatment and Constant C.D.'s.

roughly to those obtained during D.C. treatment.[1] This applies only where the C.D. is high, however ; for low current densities the efficiency of film formation decreases, the rate of decrease being appreciably more rapid than in the case of D.C.

Fig. 72 shows the increase in weight of aluminium test-pieces of 100 cm.^{2} surface, in grams per kilowatt-minute, for different electrolyte concentrations with D.C. and A.C. With the exception of the values in the very dilute solutions the efficiency (g./kW.-min./cm.^{2}) during D.C. electrolysis is considerably better than in

[1] Cf. Figs. 62, 63 and 64.

the case of A.C. treatment. Further, in the region investigated the efficiency increases as the current density increases in A.C. oxidation, whilst the reverse is the case in D.C. electrolysis.

In the case of constant current treatment with both D.C. and A.C., one of the most vital factors is the dissolution of the already formed film; this is only slightly affected by the concentration of the oxalic acid. Naturally the solution process is more pronounced where the film forms slowly; and in this case the loss of energy is great. This is the principal reason for the inferiority of A.C. treatment compared with D.C. electrolysis. Another disadvantage of A.C. where two aluminium electrodes are used is that the already formed

Fig. 72.—Gain in Weight of Aluminium in g./kW.-min./100 cm.^{2} in relation to the Concentration of the Oxalic Acid (per cent.) for D.C. and A.C. Treatments.

film offers resistance to the passage of the current, even during the negative half-period. Finally, the oxygen set free at the electrodes, which does not enter into the formation of the film, has to be taken into account as a factor reducing the efficiency, even if it is of only secondary importance. The lower efficiency of A.C. electrolysis compared with D.C. treatment, therefore, appears to be fully explained. In both cases, however, the efficiency increases as the oxalic acid concentration is increased, principally because the average voltage decreases in concentrated solutions.

The increase in weight, the increase in thickness of the films and the decrease in thickness of two aluminium sheets, each of 50 cm.^{2} surface area, are shown in Figs. 73 to 75, for constant voltages and one hour's treatment with A.C. Oxalic acid was again

used for the electrolyte, the solutions ranging from 0·36 to 5·71 per cent. in concentration. The voltages employed were 40 to 100, the frequency being 50 cycles per sec. At 90 and 100 v. marked rises in temperature were observed shortly after the current was switched on. The increase in thickness of the film and the decrease in the thickness of the aluminium were so small as to be unmeasurable below 60 v. The general tendency of the variation in weight and thickness was almost the same as in D.C. treatment, but here also the disadvantageous effects of rise in temperature, of solvent action and of unproductive oxygen evolution were apparent.
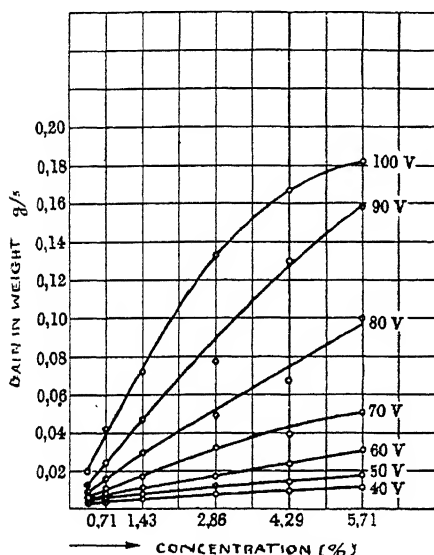
FIG. 73.—Increase in Weight of Aluminium in relation to Concentration of Oxalic Acid (per cent.) during Treatment with Constant Alternating Voltages.
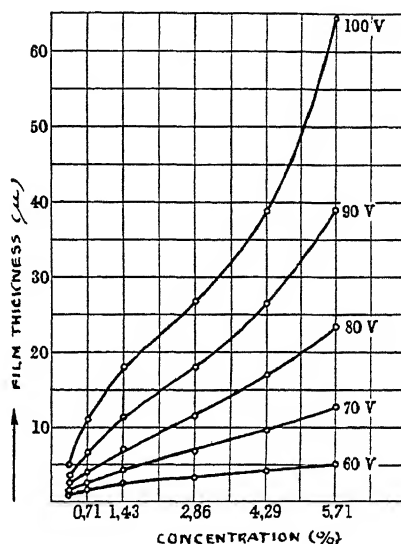
FIG. 74.—Growth in Film Thickness in relation to Concentration of Oxalic Acid (per cent.) during Treatment with Constant Alternating Voltages.

In Fig. 76 the curves for the increase in weight per kW.-min./100 cm.^{2} as a function of the concentration of the electrolyte, the voltages being maintained constant, for D.C. and A.C. treatment respectively, are placed together for purposes of comparison. These curves show that D.C. electrolysis reaches its highest efficiency at 60 v. in 4 to 6 per cent. oxalic acid solution.

(c) Growth of the Film where D.C. is Superimposed on A.C.

In a foregoing section of this book we have already discussed combined D.C.-A.C. treatment by the superimposition of the two types of current. We shall report in the following on some

experiments which were carried out to observe the nature of the film formation with this type of treatment. The tests were made using a circuit of the type shown in Fig. 49.[1] The aluminium electrodes A shown in this figure had a surface of 50 cm.[2] each; the electrolyte was a 1·43 per cent. solution of oxalic acid, which was renewed after each separate test of the series was completed.

The magnitudes of the current passing through the cell when A.C. and D.C. are superimposed depend on the voltages and on the time; the direct current is not only dependent on the direct voltage,
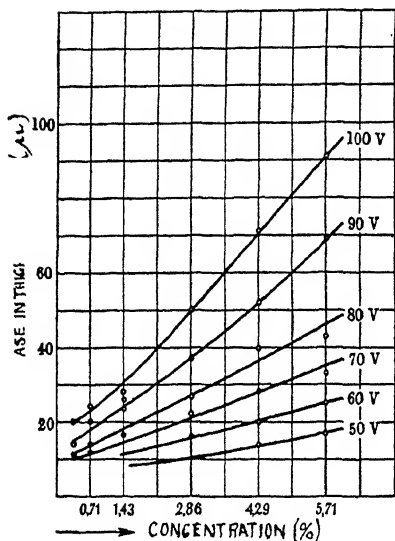
FIG. 75.—Decrease in Thickness of the Aluminium in relation to the Concentration of Oxalic Acid (per cent.) at Constant Alternating Voltages.
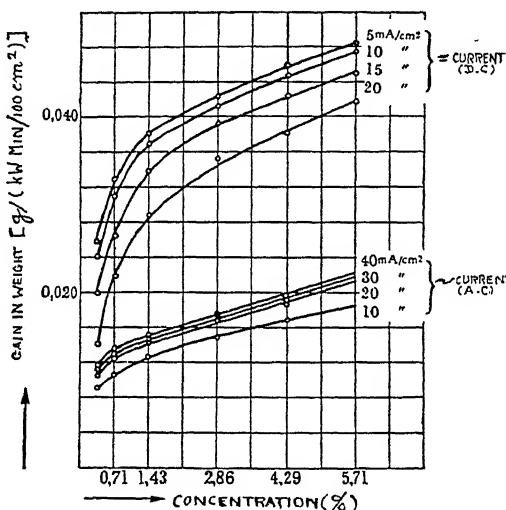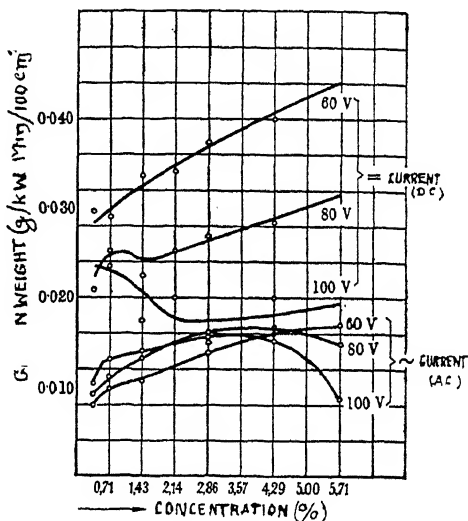
FIG. 76.—Gain in Weight of the Aluminium in g./kW.-min./100 cm.[2] in relation to the Concentration of Oxalic Acid (per cent.) for D.C. and A.C. Treatments at Different Constant Voltages.

however, but also on the alternating voltage; and, similarly, the alternating current is affected by the direct voltage. Accordingly, the tests were carried out in the following manner:

A.—When a constant direct voltage was applied, the alternating voltage was chosen so that a constant alternating current passed through the cell. In this case the direct current varied during the electrolysis.

B.—When a constant alternating voltage was applied, the direct voltage was chosen so that a constant direct current passed through the cell. In this case the alternating current varied during the treatment.

[1] Cf. p. 115.

The tests showed in the first place that, with D.C. of 60 v. on which an A.C. of current density 20 ma./cm.² was superimposed, the films produced had a better protective effect against corrosion than the films produced with the other current types used in this series of tests. Under similar experimental conditions (60 v.) the influence of the concentration on the formation of the film was next determined. Alternating current of different current densities (10, 20 and 30 ma./cm.²) was superimposed on direct current at 60 v., and oxidation was carried out in 0·36, 1·43,
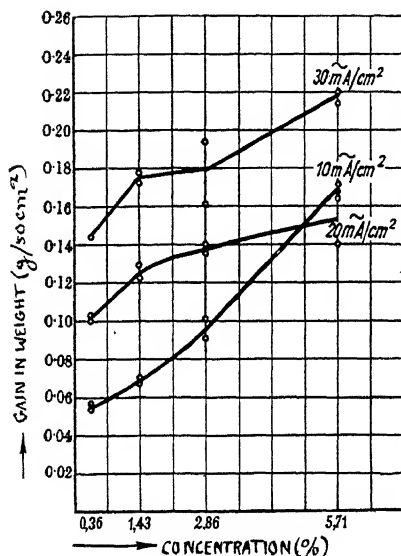
FIG. 77.—Gain in Weight of the Aluminium in relation to the Concentration of Oxalic Acid (per cent.) for Constant Voltage (60) D.C. and Superimposed A.C. of Different Current Densities.
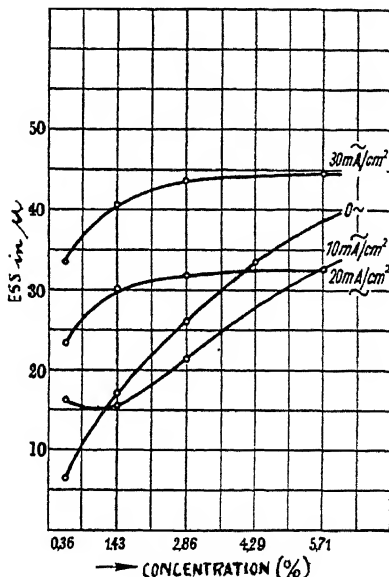
FIG. 78.—Growth in Thickness of Film in relation to the Concentration of Oxalic Acid (per cent.) for Constant Voltage (60) D.C. and Superimposed A.C. of Different Current Densities.

2·86 and 5·71 per cent. solutions of oxalic acid for an hour in each case. Figs. 77 and 78 indicate the increase in weight and thickness of the films. As the electrolyte concentration increased, the film thickness also increased. If, however, the superimposed A.C. was of high current density, the tendency to grow decreased markedly with the concentration, as is particularly clearly shown in the curves representing the film thickness (Fig. 78).

F. Wöhr has investigated the influence of the frequency of fully-rectified A.C.[1] He found that the frequency of the current had little influence on the film thickness. After 8 hours' oxidation of

[1] *Cf.* Fig. 50, p. 115.

aluminium in 3 per cent. oxalic acid the following film thicknesses were obtained :

Hertz	μ
50	109
1,000	113·5
10,000	125
100,000	103

We shall discuss elsewhere the influence of the frequency on the breakdown voltage of the film.

D.—Influence of Temperature on the Growth of the Film

We have repeatedly referred to the deleterious effect of high temperatures of the electrolyte or of the electrode on film formation.[1]
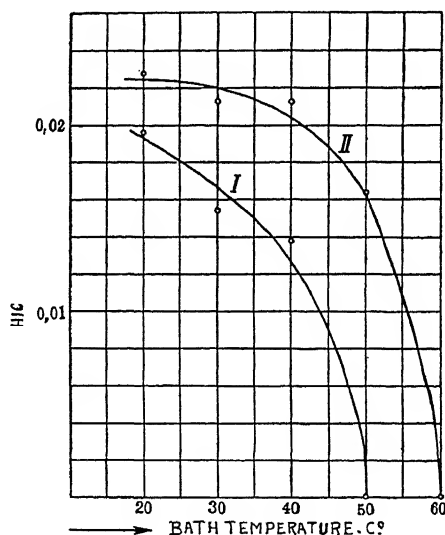
Fig. 79.—Influence of the Temperature of the Electrolyte on the Film Thickness.

A comprehensive investigation of the influence of temperature was carried out in 1·43 per cent. solutions of oxalic acid at temperatures of 20°, 30°, 40°, 50° and 60° C., using D.C. and A.C. treatments, the former with current densities of 12 ma./cm.², and the latter with 40 ma./cm.² Using D.C., films could no longer be obtained at temperatures above 50° C. ; the limiting temperature was 60° C. in the case of A.C.   Fig. 79 shows the film thicknesses for D.C. (*1*) and A.C. (*II*) in relation to the temperature.   The rapid decrease in

[1] *Cf.* pp. 81, 83 and 96.

thickness of the film as the temperature rises is clearly shown by the curves.

E.—Influence of the Composition of the Metal on the Film Thickness

The thickness of the oxide film is to a large extent dependent on the composition of the basis metal. The films on alloys containing copper are the thinnest, since the copper compounds produced at the anode in the acid electrolytes used commercially are considerably more soluble than aluminium oxide. Under ordinary conditions of working, films of thickness greater than 15 to 20 μ cannot be obtained on duralumin. The thickness of the films obtainable on Silumin is also not so great as in the case of pure aluminium, since
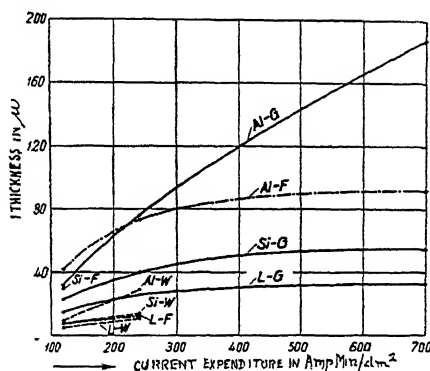
FIG. 80.—Relation between Film Thickness and Current Expenditure for Various Materials and Types of Current.

the silicon, which is present as a fine-grained, heterogeneous and insoluble constituent in the aluminium oxide, is removed by the acid electrolyte when the oxide undergoes solution. This means that the attackable surface of the aluminium oxide is increased, and therefore its solution is accelerated. The finely divided silicon, which is insoluble in the electrolyte, remains suspended in the liquid, and only slowly settles to the bottom.

H. Schmitt has investigated the growth of the film for equal current expenditure and using different types of current in the cases of Lautal (*L*), Silumin (*Si*) and pure aluminium (*Al*), and has found that with all types of current the film is thinnest on Lautal and thickest on pure aluminium, that on Silumin occupying an intermediate position.

Fig. 80 shows the increase in thickness of the films on the above-mentioned light metals for D.C. (*G*), A.C. (*W*) and rectified high-frequency current (*F*) as a function of the current expenditure.

Table XXII[1] shows the difference in the growth in thickness on aluminium and duralumin in electrolytes containing 25 and 42 per cent. by weight of sulphuric acid respectively.

In spite of the application of the same voltage, the current density is in both cases, with the 25 and with the 42 per cent. sulphuric acid, greater for duralumin than for aluminium. In the first case the current expenditure (amp.-min./dm.^{2}) is only about 10·5 per cent. greater for aluminium than for duralumin, whilst the film thickness on the aluminium exceeds that on the duralumin by 158 per cent. In the second case, in spite of the C.D. being about 26 per cent. greater with duralumin, the film on the aluminium is some 107 per cent. thicker than that on the duralumin. This great difference in the growth in thickness on the two metals is due to the

<div align="center">TABLE XXII[1]</div>

25 per cent. H_2SO_4, 20-21°C., 15 v.	C.D., amp./dm².	Time, mins.	Current Expenditure, amp.-min./dm².	Film Thickness, μ.
Aluminium	2·1	40	84·0	24·25
Duralumin	2·53	30	75·9	9·4
42 per cent. H_2SO_4, 20-21°C., 12·5 v.				
Aluminium	2·17	40	86·8	36·5
Duralumin	3·66	30	109·8	17·6

copper content of the duralumin and the ready solubility of the copper oxide and/or copper sulphate formed during the oxidation. We shall come across similar examples in connection with our discussion of the influence of the basis metal on the resistance to abrasion of the films.[2]

F.—Composition of the Oxide Films

The films produced electrolytically on aluminium or its alloys may contain, in addition to aluminium oxide with a greater or lesser water content, constituents of the electrolyte or of the particular alloy.

Thus, the films produced in dilute sulphuric acid almost invariably contain some sulphuric acid. The films derived from chromic acid as a rule take up small quantities of chromium oxide, which may impart a greyish to deep black coloration to the film. The films

[1] Based on researches by Messrs. Siemens & Halske A.-G.
[2] Cf. Table XXIII, p. 142.

produced on pure aluminium or on one of its alloys in the same electrolyte frequently differ, even in appearance, so markedly from one another that definite conclusions can be drawn regarding the nature of the basis metal. Silumin always gives rise to more or less grey-coloured films, which may be very deep in tone, in different electrolytes, the colour being due to the finely divided silicon entrapped in the film. Alloys containing copper give rise in oxalic acid to films which present a characteristic bluish-white lustre attributable to the copper content; whilst oxide films on pure aluminium produced in this electrolyte have a light straw-yellow to deep yellow colour, according to the thickness of the film.

In considering the composition of oxide films a distinction must, therefore, be drawn between films which contain no impurities or constituents derived from the electrolyte or the basis metal, in addition to the aluminium oxide or hydroxide, and those which have taken up accidental impurities from the surrounding media. Any discussion of the typical chemical composition of oxide films will, therefore, best be served by investigations on films of the first type, that is to say, those produced on pure aluminium, which have not taken up any impurities from the electrolyte.

W. G. Burgers, A. Claassen and J. Zernicke carried out chemical and X-ray investigations on the film produced anodically on aluminium in borax-boric acid solutions at 500 v. and 100° C.; they found it to consist of pure aluminium oxide with a small water content. On heating to 1200° C. the loss in weight was of the order of 5 per cent. The oxide was in a form related to the cubic γ-oxide. A. Güntherschulze oxidized aluminium in boric acid solution with small additions of borax up to voltages of 750. The increase in weight of the test-piece was 67·3 mg. After drying for 2 hours at 100° C. the loss in weight was found to be 1·2 mg., and after heating for one hour at 450° C. a further loss of 1·3 mg. occurred. If the film had had the composition of the hydroxide, $Al(OH)_3$, the latter decrease in weight at 450° C. should have amounted to 23·3 mg. It was not possible to detect any boron in the film, and A. Günther-schulze thus demonstrated that the film consisted of aluminium oxide with a water content of about 2 per cent. From the results of X-ray investigations, G. Wassermann and E. Schmidt reached the conclusion that even in the film formed in oxalic acid solution there is actually only one line which is identical with that of the strongest line of γ-Al_2O_3. After strong heating, the film consists of very fine-grained, but already crystalline, γ-Al_2O_3. E. Belwe considered that the films produced electrolytically on aluminium consist of very fine γ-Al_2O_3.

C. Aribault has investigated the film produced by the Bengough and Stuart process[1] in chromic acid solution and found it to contain

[1] *Cf.* p. 190.

0·041 mg. of chromic oxide per square metre of surface.   In the films produced anodically on aluminium in dilute sulphuric acid H. Jackson estimated the SO_3 content to be about 13 per cent., and this result agrees with that obtained by K. Norden.[1]

The oxide films produced in solutions of organic acids consist exclusively of aluminium oxide with a varying water content, since the organic acids are oxidized at the anode to carbon dioxide; after the usual washing of the film there are, therefore, practically no detectable traces of acid.   Different authors are in agreement in estimating the water content of the films produced in oxalic acid as about 15 per cent. and the aluminium content as about 45 per cent. ; this would give the film the composition $Al_2O_3 . H_2O$. According to Burgers, Claassen and Zernicke, analyses carried out by J. A. M. van Liempt gave the same results for a film produced in potassium dichromate-sulphuric acid solution. .

The investigations which have been made show that the composition of electrolytically produced aluminium oxide films is not uniform, but is to a very large extent dependent on the method of production.

[1] *Cf.* p. 77.

SPECIAL PART.

CHAPTER VIII

THE PROPERTIES OF ALUMINIUM OXIDE FILMS

It has been repeatedly shown in the foregoing chapters that the properties of anodically produced films with which we shall deal are to a great extent dependent on the oxidation process. According to the type of current, the current density or voltage, the nature, concentration and temperature of the electrolyte, and the period of treatment, the films obtained on pure aluminium may be thin or thick, hard or soft, and possessed of a very high or a very low rectifying effect. A further factor of extreme importance for the properties of the film is the composition of the basis metal itself. After what has been said, no further explanation is required of the fact that the constituents in the alloys play an essential part in the determination of the properties of the film.

Specific Gravity

In spite of the fact that different methods have been used, results in good agreement have been obtained for the specific gravity of anodically produced films. Certain authors have calculated the density from the increase in weight and decrease in thickness of the aluminium, and the thickness of the film (produced in oxalic acid). Since the film, which is honeycombed by numerous pores, cannot be considered as a homogeneous body, calculation gives only the apparent specific gravity, which is in the region of 3. In another article the specific gravity of a film produced in aqueous oxalic acid on aluminium is given as 2·76. Burgers, Claassen and Zernicke, using the suspension method, found the specific gravity of a film produced in a boric acid-borax bath to be 3·10 ± 0·05.

Hardness : Abrasion-resistance

The hardness of an oxide film depends both on the nature of the basis metal and on the conditions of production. The hardness may be determined by the usual hardness-testing methods, but difficulties are presented both in the case of thin and thick films : in the first case, the thin, hard film on the softer underlying metal is readily impressed ; and in the second case, where thick films

are tested, the considerable difference in hardness between the harder portion of the film next to the metal and the softer portion of the film which has been in contact with, and to some extent changed by, the electrolyte has to be taken into consideration. According to an article by J. E. Lilienfeld *et al.*, W. H. Coulter has shown that the hardness of a film decreases along an axis perpendicular to the metal surface proportionally to the distance from the metal, which is a consequence of the loosening effect which the electrolyte exerts. Coulter carried out his hardness measurements on films produced on aluminium in dilute sulphuric acid, and he found that the hardness fell off in the ratio of 50 to 1 as the distance increased from the basis metal to the outer surface.

For the reasons stated, the results obtained by Martens using the scratch method did not yield reliable results. In this method of testing, a diamond is impressed on the object under test, and the object is moved horizontally, whereby, with sufficient load, a scratch is left on the material ; the scratch-hardness is estimated from the width of the scratch, which is measured microscopically, taking into account the load employed. The values obtained vary widely and can be considered only as approximations. Measured on the Mohs scale the hardness of a film produced on aluminium by D.C. in oxalic acid is 7 to 8, so that the film lies between quartz and topaz in hardness.

A process developed by Siemens and Halske A.-G. for the determination of the abrasion-resistance gives more reliable results than the above-mentioned processes and yields figures which are truly comparable. The process depends on the following principle : the oxidized test-piece is moved to and fro under a hard metal pointer which presses on it under a constant weight (300 grams) until the electrically insulating film is penetrated, thereby closing a relay circuit, which stops the motor operating the device. The number H of the double movements which the test-piece has made, which is shown by an. indicator, is the absolute measure of the abrasion-resistance. Comparable values are obtained only if the film thickness δ in microns is simultaneously determined. From the values of H and δ the specific abrasion-resistance h can be determined, thus :

$$h = \frac{H}{\delta},$$

i.e. the value of H (which is the number of double movements) per micron of film thickness.[1] In spite of the considerable differences between individual determinations the process gives good comparative values.

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[1] If the hardness of the film is not uniform at different distances from the basis metal, the ratio H/δ represents the average abrasion-resistance.

Table XXIII collects the results of measurements of the abrasion-resistance on five films produced on aluminium and on some commercial alloys by different processes.[1]

The values in Table XXIII show that in general the thicker films also exhibit greater specific abrasion-resistance. This does not mean that there is any rigid law from which it would follow that the film thickness *per se* determines the abrasion-resistance, as can be seen by comparing the results obtained on Lautal: the smallest value of $\frac{H}{\delta}$, namely 170, was obtained in this case with a film thickness of 7·3 μ for the GXh film, which gave a specific abrasion-resistance of 20, but the value 500 for H and film thickness 3·8 μ

FIG. 81.—Specific Abrasion-resistances of Various Films on Aluminium and Aluminium Alloys.

with the GX film corresponded to the comparatively high specific abrasion-resistance of 130.

The highest values for H are shown by the GS film on 98-99 per cent. aluminium at 468,300, and by the GXh film on Hydronalium Hy 7 at 459,200. Dividing by the respective film thicknesses of 31·8 and 35·3 μ the specific abrasion-resistances are found to be 14,700 and 13,000.

Influence of the Composition of the Basis Metal and of the Oxidation Process on the Specific Abrasion-resistance

In order to give a better picture of the results shown in Table XXIII the specific abrasion-resistances are represented diagrammatically in Fig. 81 (which omits the results obtained with Lautal

[1] Tests made by Messrs. Siemens & Halske A.-G.

TABLE XXIII.—ABRASION-RESISTANCE AND THICKNESS OF OXIDE FILMS ON ALUMINIUM AND SOME ALUMINIUM ALLOYS

Material.	Nature of Current.	Electrolyte.[1]	Process.[1]	Abrasion-resistance, number of double movements H.	Film Thickness δ, microns.	Specific Abrasion-resistance, $H/\delta = h$.	Period of Treatment, minutes.
Aluminium, 98–99 per cent.	D.C.	sulphuric acid	GS	468,300	31·8	14,700	40
	D.C.	oxalic acid	GX	228,000	24·6	9,300	45
	D.C.	,, ,,	GXh	162,300	20·9	7,800	50
	A.C./D.C.	,, ,,	WGX	51,300	17·3	3,000	40, 15
	A.C.	,, ,,	WX	13,300	9·3	1,400	40
Duralumin	D.C.	sulphuric acid	GS	51,200	11·7	4,400	40
	D.C.	oxalic acid	GX	1,600	2·9	550	45
	D.C.	,, ,,	GXh	1,300	5·5	240	30
	A.C./D.C.	,, ,,	WGX	5,900	9·4	630	40, 15
	A.C.	,, ,,	WX	390	8·9	40	40
Hydronalium, Hy 7	D.C.	sulphuric acid	GS	44,000	11·7	3,800	45
	D.C.	oxalic acid	GX	273,300	24·6	11,100	45
	D.C.	,, ,,	GXh	459,200	35·3	13,000	60
	A.C./D.C.	,, ,,	WGX	11,700	11·7	1,000	40, 15
	A.C.	,, ,,	WX	4,300	5·9	730	40
Lautal, 14 VN	D.C.	sulphuric acid	GS	1,800	11·7	150	40
	D.C.	oxalic acid	GX	500	3·8	130	45
	D.C.	,, ,,	GXh	170	7·3	20	60
	A.C./D.C.	,, ,,	WGX	340	8·7	40	40, 15
	A.C.	,, ,,	WX	1,200	8·1	150	40
Legal 2	D.C.	sulphuric acid	GS	133,200	14·7	9,100	40
	D.C.	oxalic acid	GX	149,400	16·3	9,200	45
	D.C.	,, ,,	GXh	144,700	16·3	8,900	60
	A.C./D.C.	,, ,,	WGX	31,700	8·8	3,600	40, 15
	A.C.	,, ,,	WX	9,400	5·9	1,500	40
Pantal	D.C.	sulphuric acid	GS	191,800	14·7	13,100	40
	D.C.	oxalic acid	GX	72,300	8·8	8,200	45
	D.C.	,, ,,	GXh	299,900	32·4	9,300	60
	A.C./D.C.	,, ,,	WGX	43,600	9·1	4,800	40, 15
	A.C.	,, ,,	WX	5,800	5·9	980	40
KSS	D.C.	sulphuric acid	GS	179,800	14·7	12,200	40
	D.C.	oxalic acid	GX	223,000	20·6	10,800	60
	D.C.	,, ,,	GXh	202,300	20·6	9,800	60
	A.C./D.C.	,, ,,	WGX	67,600	14·7	4,600	40, 30
	A.C.	,, ,,	WX	10,300	8·8	1,200	40
Wicromal	D.C.	sulphuric acid	GS	113,800	17·6	6,500	40
	D.C.	oxalic acid	GX	79,600	20·6	3,900	60
	D.C.	,, ,,	GXh	163,100	20·6	7,900	60
	A.C./D.C.	,, ,,	WGX	181,700	14·7	12,300	40, 30
	A.C.	,, ,,	WX	1,100	5·9	190	40

[1] Details of the processes and of the standard conditions of oxidation will be found in Table XXXIV, p. 189.

because of the smallness of the values). The diagram makes it apparent that in the case of all the metals the A.C. films (WX) give the smallest specific abrasion-resistance values ; the A.C. film on Lautal (*cf.* Table XXIII) is, however, an exception, its specific abrasion-resistance being the same as that of the GS film, and even greater than the specific abrasion-resistance of the oxalic acid D.C. film (GS). The A.C. films do not, therefore, affect the impression of very great irregularity which is suggested by a first glance at the diagram.

The highest values for the abrasion-resistance which have been observed up to the present were obtained on a magnesium-rich aluminium alloy (Stalanium), which is not included in Table XXIII.[1] A film produced in 5 per cent. oxalic acid solution at 70 v. (3·5 amp./dm.^{2}, 18° C., 60 min.) on this alloy was not penetrated even after 2,349,000 double movements when tested by the abrasion-resistance method described above. High abrasion-resistances of more than 700,000 have also been obtained on cast Pantal oxidized in 5 per cent. oxalic acid with the voltage maintained at 80 v.[1] It can be seen, therefore, that the magnesium content in general exerts a favourable influence on the abrasion-resistance, in the case of the films produced by D.C. both in oxalic acid and in sulphuric acid, as the values for Pantal, Legal 2 and KSS in Fig. 81 indicate. An exception is presented by the D.C. sulphuric acid film (GS) on Hydronalium Hy 7, which possesses a small resistance compared with the other D.C. films (GX and GXh) on this alloy.

In contrast to the very hard D.C. films produced in general on magnesium-containing alloys the D.C. films obtained in oxalic acid on copper-containing alloys, such as duralumin and Lautal, have very low values, in respect to both the specific abrasion-resistance and the film thickness. These films exhibit the bluish lustre, due to the copper content, which has already been referred to. Presumably, in addition to the copper content, the coarsely porous structure of these films is responsible for their small abrasion-resistance. The comparatively high value of H (51,200) and the high specific abrasion-resistance (4,400) of the D.C. sulphuric acid film (GS) on duralumin compared with the lower corresponding values (1,800 and 150) on Lautal, while the film thickness remains the same (11·7 μ) on the two alloys, should be noted. In the same way as copper, the presence of zinc reduces the hardness, as does also a high content of silicon (13 per cent.).

In the case of four of the eight metals under discussion the D.C. sulphuric acid film (GS) is specifically harder than the other films on the same metal (aluminium, duralumin, Pantal, KSS). In the case of Legal 2 the difference between the abrasion-resistance of this film and that of the other D.C. films (GX, GXh) on this alloy

Values obtained by Messrs. Siemens & Halske A.-G.

is very small, and in the case of Lautal the abrasion-resistance of the GS film and the WX film is the same. In the case of Hydronalium Hy 7 the GS film is far behind the other D.C. films so far as the specific abrasion-resistance is concerned, and the same applies to the GX film on Wicromal. In the case of the latter alloy it is surprising that, and not immediately clear why, by far the highest specific abrasion-resistance is exhibited by the A.C./D.C. film (WGX), and this is the more remarkable in that the WX film on this alloy exhibits a particularly low specific abrasion-resistance. It should be noted in this connection that the A.C./D.C. films produced in oxalic acid on other metals, although in general appreciably harder than the A.C. films, in no case have greater specific abrasion-resistances than the oxalic acid D.C. films. To what extent this peculiar phenomenon is due to the manganese content, to the thorium content, or to the joint presence of both alloying constituents, can be determined only by systematic investigations.

The more important results discussed above may be summarized as follows :—

1. The films produced by A.C. in oxalic acid in general exhibit the smallest specific abrasion-resistance, which is less than that of the other films on the same metal. The WX film on Lautal is an exception to this.

2. The copper-containing alloys (duralumin, Lautal) in general give appreciably lower specific abrasion-resistance than the copper-free alloys. The greatest abrasion-resistance among the copper-containing alloys is found in the case of the GS film on duralumin.

3. In the alloys of aluminium in which magnesium is a predominating constituent there is in general a tendency to form films which possess good abrasion-resistance when D.C. treatment is used. The GS film on Hydronalium Hy 7 is an exception to this.

4. In the case of four out of the eight metals investigated the specific abrasion-resistance of the GS film is greater than that of the other films on the same metal. In the remaining four metals the specific abrasion-resistance of the GS film is either equal to or less than that of the other D.C. films on the same metal.

5. Of the films on Wicromal the WGX film exhibits an unexpectedly high abrasion-resistance.

It is not possible to draw any definite conclusions regarding the influence of the composition of the basis metal or of the oxidation process on the specific abrasion-resistance of oxide films from the knowledge which obtains on this subject up to the present. Certain experimental facts present the possibility of estimating, from the composition of the aluminium alloy, and from the particular process of oxidation employed, the type of abrasion-resistance which may be expected. In the present state of our knowledge the actual

results obtainable with an alloy not previously investigated can be gauged only by direct experiment.

Flexibility : Deep-drawing Qualities

The hard films are naturally brittle, so that when the underlying metal is even slightly bent cracks arise in the film ; these cracks are, however, so fine that they close up again when the metal is bent back, and the film does not scale off, even when the material is repeatedly bent to and fro.   In connection with the use of anodically oxidized wires in electric windings the flexibility is of great importance, and numerous proposals have been made with the object of rendering hard films pliable, either by chemical treatment with weakly alkaline solutions, or else by the use of A.C. during the actual oxidation process.   Dilute water-glass solutions as electrolyte have proved of value for such purposes.[1]   A further means of rendering films flexible consists in raising the temperature of the electroylte.   In this way it is possible to arrive at various gradations of hardness and pliability.   The above remarks regarding the flexibility of films apply directly to the deep-drawing qualities ; these are, moreover, necessarily bound up with the use of sufficiently soft films.   In general, in the present state of technical development it is preferable to undertake any forming processes on an object before oxidation.

Resistance to High Temperatures

As would be expected from their chemical nature, and from the high melting-point of aluminium oxide (in the region of 2000° C.), the films are extremely resistant to heat.   The only limitation on the heating which they will stand is that imposed by the lower melting-point of the aluminium (659° C.) or of the particular aluminium alloy.   Very hard films tend to give rise to hair cracks at comparatively low temperatures ; the thicker the film the more marked become these fine cracks.   In thick films produced in oxalic acid on aluminium they may even be observed on heating to 80° C., in consequence of the different coefficients of expansion of the metal and of the film.   Scaling off of the film never occurs, however, as a consequence of crack-formation, even if the temperature is raised to the melting-point of the metal.   In the more pliable and thinner films produced in oxalic acid or sulphuric acid on duralumin, crack-formation is not observed at 80° or 100° C.

Adherence

The adherence of the oxide film to the basis metal is, if the oxidation is properly carried out, so good that it is scarcely possible

[1] According to researches by Messrs. Siemens & Halske A.-G.

to separate the film from the underlying surface by mechanical means : for the film is actually intergrown, during oxidation, in the metal. Special chemical or electrochemical means are necessary to remove the film.

A method frequently used to bring about separation for purposes of analysis consists in heating the oxidized test-piece in a current of dry hydrogen chloride or chlorine.[1] The aluminium is in this way converted into aluminium chloride, which volatilizes at the high temperature employed and sublimes in the cold portion of the reaction tube. In another method, proposed by Wernick, the test-piece, with the film on it, is first immersed in a saturated mercuric chloride solution, and then for a few seconds in metallic mercury, after which it is immersed in distilled water, in which part of the film separates off after some hours. A valuable method of removing the film from the metal consists in making the test-piece the cathode, either in the electrolyte used to produce the film or in a different solution, a high current density being employed. Alternate cathodic and anodic treatment produces the same effect.

Colour of Oxide Films

If aluminium or one of its alloys with a polished surface is given only a short oxidation treatment, for seconds or a few minutes, according to the current density employed, the film formed is in the first place invisible to the naked eye. After a certain thickness is attained, interference colours, which have already been referred to, appear. All the colours of the spectrum repeatedly become visible in turn as the film thickness increases, until when the thickness has grown to a certain value they disappear. This phenomenon can be particularly well observed with tantalum and with certain aluminium alloys, such as Anticorodal, if a strip of the metal is slowly removed from the electrolyte during oxidation. Very beautiful colour effects may be produced in this way on polished objects.

It is possible to speak of the intrinsic colour or colour proper of the film only when the thickness has exceeded a certain degree, up to which point interference colours occur. The intrinsic colour of the film is dependent on the thickness of the film, on the nature of the basis metal and its previous treatment, on the nature of the electrolyte and on the other conditions of oxidation.

If the film in itself is colourless and transparent, as in the case of the film produced by D.C. in sulphuric acid, the thickness has no effect on the colour. The films on silicon-containing alloys present an exception to this, since, as has been mentioned earlier, they are greyish-coloured. The alloys containing manganese, also,

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[1] The use of chlorine for this purpose was introduced by Messrs. Siemens & Halske A.-G.

frequently give rise to greyish tones. In the case of these alloys, therefore, increasing film thickness gives rise to an intensification of the coloration. The films produced in oxalic acid with D.C. possess a yellowish colour. This is not due to the presence of iron, which invariably occurs in commercial aluminium, as might be conjectured, since it has been found that the film produced on refined 99·9 per cent. aluminium in oxalic acid also possesses the characteristic yellowish shade. The oxalic acid film produced with D.C. is, as long as it is thin, a light straw yellow ; as the thickness increases, the yellow colour becomes more and more intense. On alloys containing copper, the film, as already mentioned, exhibits a bluish lustre. The silicon-containing alloys give grey films also when treated in oxalic acid. The films produced by D.C. in chromic acid by the Bengough and Stuart[1] process are opaque in consequence of the small chromium oxide content, and are coloured grey to a greater or lesser extent.

With A.C. treatment in sulphuric acid the colours are approximately the same as with D.C. oxidation, but A.C. is comparatively rarely used. In oxalic acid, A.C. treatment gives rise to films which are coloured brass-yellow to gold and bronze on pure aluminium and the majority of its alloys, the shade being dependent on the current density and the period of treatment. Here again, the alloys containing silicon are exceptional and preserve their grey colour. In the case of some alloys, such as KS-sea-water and BS-sea-water, scarcely yellowish shades similar to that of German silver are often obtained, possibly due to the heat-treatment which the metal has undergone. In chromic acid, using A.C. under suitable conditions in the manner proposed by Messrs. Siemens & Halske A.-G., jet-black films may be produced on pure aluminium and its alloys ; these on analysis show a chromium content of 0·9 per cent. These films are not produced for commercial use, since their production is not very reliable.

By varying the operating conditions, for example by combining D.C. with A.C., varying the current density, raising the temperature, or varying the period of treatment, it is possible to change the intrinsic colour of the film within wide limits.

In the case of many alloys their structure has a determinative influence on the colour and on the quality of the film. In the case of the manganese-containing aluminium-magnesium alloys of the type of Hydronalium, it may happen that homogeneous films fit for use cannot be produced on the material as supplied, but that after suitable heat-treatment it is possible to produce films free from defects. The same sort of thing frequently happens with commercial aluminium, and with other alloys. If streakiness, caused by segregation at the grain boundaries and made apparent

[1] *Cf.* p. 190.

by the oxidation, is observed on the surface, suitable heat-treatment may remove or minimize it. Fig. 82[1] illustrates two oxidized test-pieces produced from the same aluminium sheet, which contained 0·8 per cent. of silicon and traces of iron. The left-hand test-piece was quenched after two hours' heat-treatment before oxidation, and the right-hand test-piece was given the same treatment followed by 24 hours' aging at 300° C. After oxidation the left-hand test-piece was coloured greyish-white, and the right-hand test-piece was brown in colour. The change brought about by aging was presumably due to precipitation of silicon. The example shows what an influence heat-treatment may exert on the intrinsic colour of an oxide film.

The appearance and colour of the oxide film may be to a large extent varied by mechanical or chemical pretreatment of the metal
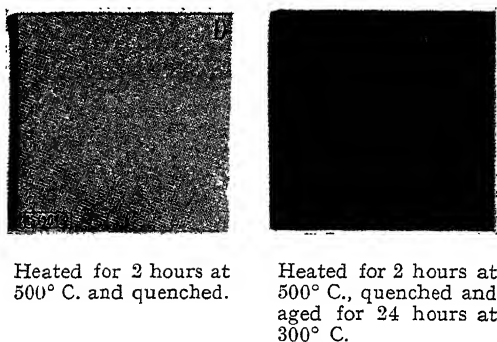

Heated for 2 hours at 500° C. and quenched.   Heated for 2 hours at 500° C., quenched and aged for 24 hours at 300° C.

FIG. 82.—[2] Influence of Heat-treatment on the Intrinsic Colour of the Film (Al + 0·8 per cent. Si).

surface. A matt-etched surface roughened by either brushing or sand-blasting always gives a matt, dull film, whose original colour is transformed from light whitish- or yellowish-grey shades to a fairly dark grey as the extent of roughening increases.

Reflectivity

Researches directed towards preserving the reflectivity of highly polished aluminium surfaces by providing them with a thin, colourless oxide film, which protects them against tarnish, are of very early date. S. Wernick has pointed out that the reflectivity of highly polished aluminium surfaces is superior to that of chromium-plated surfaces. Investigations of the life of aluminium mirrors provided with an oxide protective film have given very satisfactory results. R. Hase investigated the reflectivity of different aluminium alloys,

[1] Photographs by Messrs. Siemens & Halske A.-G.
[2] According to experiments by Messrs. Siemens & Halske A.-G.

and showed that aluminium and Polital took a better polish than other alloys, and that their reflectivity was only very slightly sacrificed when they were oxidized.   J. D. Edwards has stated that the reflectivity of commercial aluminium cannot be increased by polishing to a value over 65 to 75 per cent., but that on very hard aluminium alloys the reflectivity could be raised to 89 per cent. by special processes.   The commercial application of the latter mirror surfaces would, however, be very limited.

Aluminium given an etching treatment in a solution of 5 per cent. caustic soda and 4 per cent. sodium fluoride and subsequently immersed in an approximately 50 per cent. nitric acid solution has been found to have a slightly matt surface and to give diffuse reflection of the incident light.   In spite of this the reflectivity for visible light was maintained at 82 to 87 per cent., and for ultra-
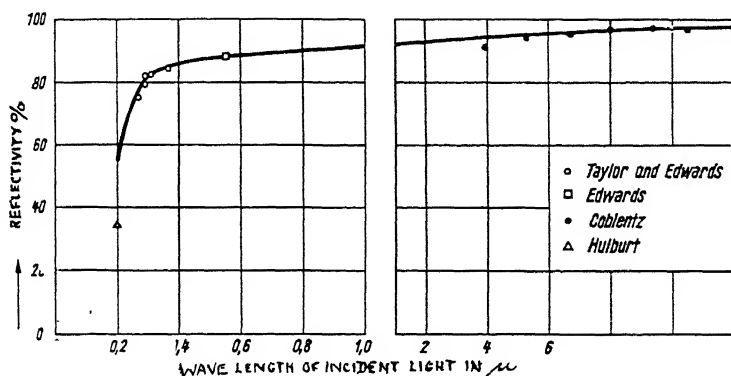

FIG. 83.—Reflectivity of Aluminium for Light of Different Wave-lengths.

violet light of wave-length 296·7 μ it was 81 to 82 per cent.   Fig. 83 shows the reflectivity for wave-lengths ranging from 0·2 to 12 μ. Infra-red light is reflected up to 97 per cent.

According to Edwards, R. B. Mason has solved the problem of producing highly reflecting, and permanent, aluminium surfaces in the following manner :   the metal, which is first highly polished, is given a preliminary anodic treatment in an electrolyte of special composition, which brings about a cleaning of the surface by removing the impurities always present in commercial aluminium, the polish being maintained, or even increased.   After this pre-liminary treatment a thin, transparent, protective film is produced on the surface by anodic oxidation in dilute sulphuric acid, and, finally, the pores of this protective film are sealed.   This process makes possible even now the production on a commercial scale of reflectors with a reflectivity of 80 to 85 per cent.   The best results are produced with high-purity, refined aluminium.

A. H. Taylor has investigated the reflectivity of aluminium with the surface treated by different processes; his tests covered a range of wave-lengths, and the results are collected in Tables XXIV and XXV.

TABLE XXIV.—REFLECTIVITY OF DIFFERENTLY TREATED ALUMINIUM SURFACES FOR LIGHT FROM A TUNGSTEN LAMP (2000° ABS.) AND ULTRA-VIOLET LIGHT (2967 Å.).[1]

Nature of Treatment.	Reflectivity, per cent.	
	Tungsten Lamp.	2967 Å.
Rolled	53	33
Turned on a lathe	83	78
Highly polished	72	56
Etched or oxidized	75–85	65–82
Polished and electrolytically brightened .	87	84
Polished, electrolytically brightened and oxidized in dilute sulphuric acid[2] . .	85	69

TABLE XXV.—REFLECTIVITY OF DIFFERENTLY TREATED ALUMINIUM SURFACES FOR LIGHT OF DIFFERENT WAVE-LENGTHS IN THE ULTRA-VIOLET.

Nature of Treatment.	Reflectivity, per cent.			
	3663 Å.	3130 Å.	3967 Å.	2652 Å.
Etched	81	80	80	76
Etched and electrolytically brightened	78	77	77	74
Polished and electrolytically brightened	87	85	84	83
Polished, electrolytically brightened, and oxidized in dilute sulphuric acid . .	79	74	69	62

Heat Emissivity

According to R. Hase, the heat emissivity of aluminium with a polished, etched or matt surface is about a tenth of that of a black body. If a thick oxide film is produced on the aluminium the heat emissivity may be appreciably increased. Fig. 84 shows the emissivity of differently treated aluminium surfaces, taking the radiation of a black body as unit, as a function of the wave-length.

[1] The Ångstrom unit (Å.) corresponds to a wave-length of 10^{-8} cm. = $0 \cdot 1$ mμ.
[2] For details of the electrolytic reflector processes, see pp. 196-200.

The curve relating to the thicker film *a* has two pronounced maxima in the region of the wave-lengths 3·8 and 6 *μ*. Whilst the maximum at 6 *μ* coincides with that of the thinner film *b*, the emission in the short-wave region in the case of the thick film *a* is greater than that of the thinner film *b*, and is many times greater than that of the unoxidized test-pieces *c* and *d*. The maximum of the emissivity at 6 *μ* falls in the region of the radiation from water and steam
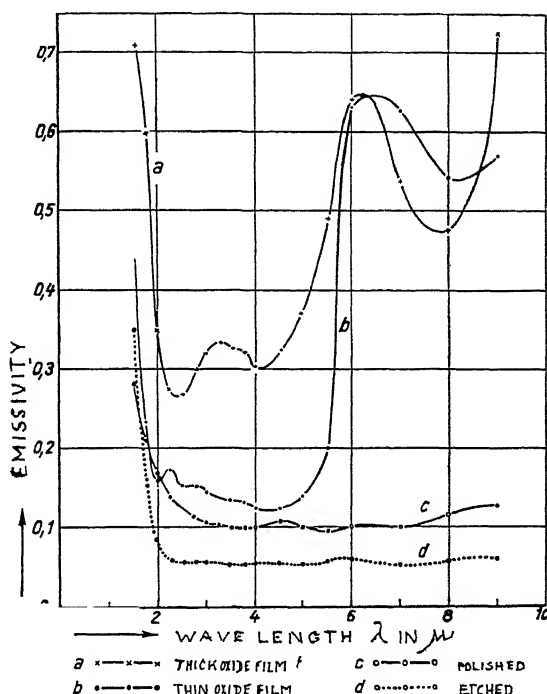
Fig. 84.—Spectral Emissivity of Oxidized, Polished and Etched Aluminium at 400° C.

radiators ; accordingly, the films are suitable for use in heating appliances and heat exchangers.

Porosity of the Oxide Films

We have seen that a certain solubility of the film in the electrolyte is a prerequisite for growth in thickness. The moderately solvent electrolyte ensures the maintenance of an adequate pore cross-section to permit the passage of the relatively large leakage current necessary for growth. In the case of these films there is no doubt of the existence of porosity. In contrast to these, the rectifying films,

which are practically insoluble in the electrolytes used for their production, exhibit a strong barrier effect and a very small leakage current, and in consequence grow to only very small thicknesses.

The whole range of gradations between these two cases of solubility and their consequent pore sizes or total pore cross-sections is possible ; and a third case is also conceivable, in which there is no measurable leakage current and in which, therefore, no pores exist in the film. This case has not, however, been actually observed either with tantalum or with aluminium or other valve metals. A leakage current, even if of a very small order, can invariably be detected. For this reason, and also as a result of investigations which permitted direct proof of the porosity of valve films, it has been concluded that all electrolytically produced oxide films are porous. On the other hand, the hypothesis has also been made that the valve films are compact, and that the existence of leakage currents is attributable to ionic or electronic conduction similar to that in non-metallic semi-conductors. These considerations are closely bound up with the problem of the mechanism of the unidirectional conduction of rectifying films, and up to the present no satisfactory explanation has been offered for these extremely complicated phenomena. It would not serve the purpose of this monograph to enter into this controversial subject, and we shall content ourselves with stating the fact that the protective films, with which alone we are concerned, are porous.

According to W. J. Müller, the metal surface, on anodic oxidation, is never completely covered, but contains a total pore surface of about 10^{-3} to 10^{-5} cm.^{2} per cm.^{2} of surface. Below this pore magnitude, further forming of the film takes place, accompanied by growth in thickness. A Simon and O. Jauch reached a similar estimate of about 10^{-5} cm.^{2} pore surface per cm.^{2} of aluminium surface for an oxide film produced in ammonium carbonate solution. Th. Rummel has photographed the cross-section of an oxidized aluminium sheet perpendicular to the surface with a linear magnification of 950 and monochromatic light. Figs. 85 and 86 reproduce these photographs and show that the pores run comparatively uniformly at right-angles to the surface. From the number of pores and the total pore volume, which was determined by means of the water absorbed by the film, Rummel calculated the diameter of the pore, assuming the cross-section to be circular, to be about 0·1 μ, whilst it was found to be about 0·075 μ from determinations of the conductivity of an aluminium sheet which was oxidized right through.

The porosity is of great importance in connection with the commercial utility of the films. It may, on the one hand, be a disadvantage, since it permits the taking up of liquids by the film, with a resultant diminution of the resistance to handling, of the

electrical insulating properties of the film, and of the protective effect towards corrosive attack. On the other hand, the absorptive power of the film may be an advantage, since it favours the taking up of dyestuffs, of photosensitive materials or of water-repelling and electrically insulating substances, which are capable of completely eliminating the above-mentioned disadvantages. Thanks to their porosity, the oxide films have also proved valuable as a basis for the adherence of paints and lacquers. According to W. Herbig, almost any paint-medium may be used on oxidized aluminium. F. Bollenrath and H. Gröber consider the film produced by anodic oxidation the best basis for the adherence of lacquers. Because of the excellent adherence obtained, considerably less paint needs to be applied on anodically oxidized parts than would be the case on
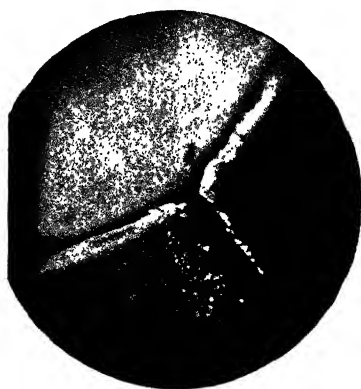

FIG. 85.   FIG. 86.

FIGS. 85 and 86.—Pores in a Cross-section of an Aluminium Oxide Film (× 950 linear magnification).

untreated metal, with considerable saving in the medium employed : the saving in weight which results is of far-reaching importance in the aircraft industry, and in the case of large aircraft may amount to several hundred kilograms.

Dielectric Constant and Breakdown Voltage

The dielectric constant ε of aluminium oxide films was determined by Güntherschulze *et al.* by different methods and was found to be about 7·45, whilst both for corundum and for precipitated Al_2O_3 the value 12 to 12·3 was obtained. H Zauscher obtained results for ε equivalent to 7·4 to 7·6 by different methods ; he showed that by carefully preventing any disturbing effects of moisture, ε increased as the temperature rose over the range from 20° to 100° C. by about 0·06 per cent. per degree.

Careful investigations of the breakdown voltage of aluminium oxide films have been made by different workers in the last few years. The individual values obtained differ widely, as a rule, so that in many cases it is necessary to take the average value of a large number of individual determinations. As far as the technical importance of the films goes, only the minimum values are of consequence; and another factor which is an important criterion of safety is the total deviation.[1]

H. Schmitt and L. Lux have determined the breakdown voltages of aluminium wires 1·3 mm. in diameter provided with oxide films
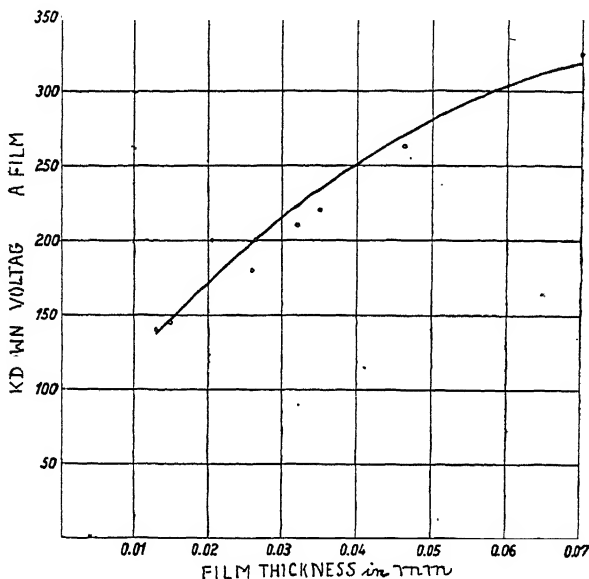
FIG. 87.—Breakdown Voltage of Oxidized Aluminium Wires 1·3 mm. in diameter in relation to the Film Thickness.

of different thicknesses. The wires were contacted with a flat polished iron plate over a length of 150 mm., the plate being loaded with 500 grams. The results obtained showed that the breakdown voltage is almost a linear function of the film thickness, as may be seen from Table XXVI and Fig. 87.

The same authors have shown that an increase in temperature up to 400° C. has only an inappreciable effect on the breakdown voltage, which falls off by some 15 per cent., so that a coil which is capable of working at 430 v. at room temperature will still exhibit a breakdown voltage of 350 v. at 400° C.

[1] According to F. Wöhr; see pp. 159 and 160.

TABLE XXVI

Film Thickness, mm.	Breakdown Voltage,		
	Maximum.	Minimum.	Mean.
0·014	160	120	140
0·015	160	130	145
0·022	200	160	180
0·021	300	190	200
0·028	208	192	200
0·030	238	196	210
0·031	240	200	230
0·048	280	250	265
0·068	340	290	325

H. Betz has also established the linear relationship between the breakdown voltage and the thickness for extremely thin aluminium oxide films.

H. Zauscher produced aluminium oxide films of different thickness in 4 per cent. oxalic acid solution at 12°-13° C., using different current densities (10-40 ma./cm.^{2}) and different forming periods ($\frac{1}{2}$ to 3 hrs.) and employing D.C. In spite of the wide variation which he introduced into the test conditions, the increase in thickness proceeded as a linear function of the quantity of electricity (Fig. 88) up to a thickness of some 55 μ. Above this limiting film thickness further growth in thickness required an increased current expenditure.[1]

FIG. 88.—Forming Curve: Film Thickness (in μ) in relation to the Quantity of Electricity (ma.-hrs./cm.^{3}).

The dielectric measurements which we are about to discuss invariably show irregularities at the same point, which fact can be explained only on the assumption that the oxide undergoes at this point a fairly rapid transition from a very porous, rather loosely coherent state to a compact state, which, naturally, tends to stop further growth in thickness.

Measurement of the breakdown voltage was carried out on carefully dried test-pieces. In one case tin-foil electrodes were used, and were pressed on the oxidized test-piece by a weight, from which they were separated by an intermediate elastic layer of hardened rubber ; in the other case point electrodes were employed,
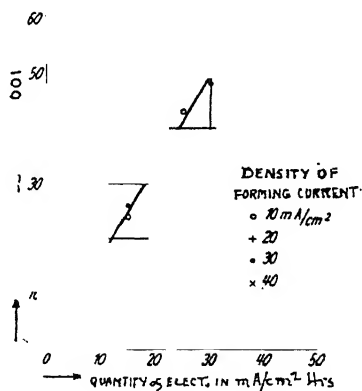
[1] *Cf.* " Spark Voltage," p. 94, Fig. 24.

sewing needles, fastened by a suitable device, being used. Curve a, Fig. 89, shows the breakdown voltages which were obtained with films of different thickness, which were free from cracks, when the tin-foil was used. The curve shows a steep rise in the region of about 44 to 62 μ. This part of the curve coincides fairly accurately
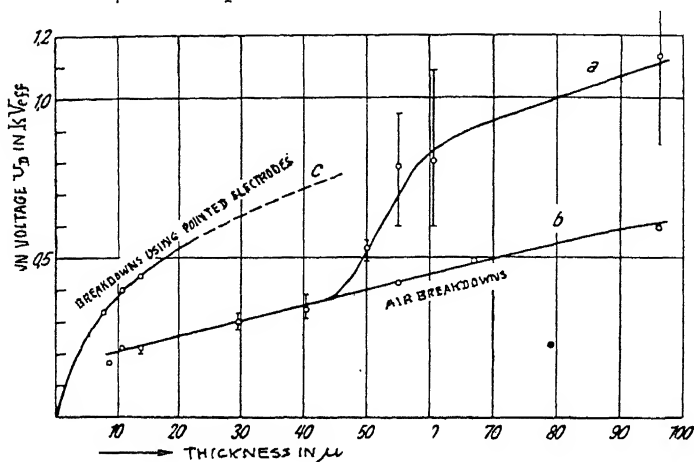

FIG. 89.—Breakdown Measurements.

with the above-mentioned limit in film thickness of about 55 μ. At this point there are two distinct types of discharge, the same phenomenon being demonstrated also by the jump in the deviation S (cf. Table XXVII) which occurs between the thicknesses 50 and

TABLE XXVII

Test-piece.	A21	L2	L4	A5	A28	27	L2	A6	A12	L8
Thickness δ in μ	8·6	10·8	13·8	29·6	40·4	50	55	60·6	96	60·8
U_D, effective volts	171	215	218	298	338	529	787	805	1134	1396
S, per cent.	—	—	4·4	5·7	8·5	5·1	16	14	20	14
S_{max}.	—	—	8·3	11	14	7·6	24	35	28	32

55 μ. The lower portion of the breakdown voltage curve a is determined by the breakdown voltage of an equally thick air layer between plate electrodes. Zauscher was able to show this by demonstrating that with plates which had thicker films, both being penetrated by cracks, breakdown invariably followed a crack and was, therefore, equivalent to air breakdown. In this way it was

possible to obtain curve b, which is a direct extrapolation of the lower part of curve a. Accordingly, it seems not improbable that this latter portion of the curve also represents air breakdown, and this supposition is supported by the fact that no difference in the breakdown voltage could be observed in the case of test-pieces with thin films, whether the films exhibited cracks or not.

Whilst, therefore, in the case of the thinner films we are dealing with the breakdown voltages of small air pores, in the case of test-pieces above the limiting film thickness the breakdown measured is that of the nearly compact oxide, which should be considered as a heat breakdown.

In the tests carried out with the point electrodes, with rise in the voltage there occurred initial air breakdowns of the type of the Lichtenberg figures, in which small sparks are given off from the needle points in rapid succession, until, on further rise of voltage, breakdown finally occurs along the shortest line joining the needle and the plate, which in most cases leads to permanent contact. These higher breakdown voltages are shown as curve c in Fig. 89. They lie considerably above the lower portion of curve a for plate electrodes, but may be considered as an extrapolation of the upper part of this curve, so that they may be regarded as the heat breakdown of the oxide for small film thicknesses. To explain this would require the assumption that the point electrodes rest in contact with only a few oxide fibres of the porous film, on which the current concentrates.

Investigations on the breakdown voltage of extremely thin oxide films on tantalum under direct voltages led G. Just to the following observation : if the tantalum was made the anode during the measurement, higher breakdown voltages were obtained than if the tantalum were the cathode. Moreover, in this case the breakdown voltage was completely proportional to the thickness of the film. Figs. 90 and 91 show the breakdown voltages obtained as a function of the film thickness. The values in Fig. 91 lie considerably lower than those in Fig. 90. In one case silver was deposited by cathode sputtering on the tantalum oxide film, for the measurement of the breakdown voltage, which gave an average value indicated by the small circle in Fig. 90. The agreement with the straight line previously obtained is excellent. On repeating this experiment with an aluminium oxide film the breakdown measurements were a failure, since the moment the smallest voltage was applied a current passed. G. Just explains this phenomenon by the existence of fine pores in the aluminium oxide film, into which the silver, in the extremely fine state of division produced by sputtering, can penetrate, short-circuiting being thus produced. The existence of pores in the film was attributed by Just to inadequate purity of the metal. It is doubtless difficult to remove the final traces of iron and silicon,

and this fact may mean that the formation of an oxide film is prevented at certain points, so that fine capillaries are produced.

J. W. Holst, and H. Zauscher repeated the tests with direct voltages and confirmed the directional effect observed by Just. When the basis metal was made the positive pole the breakdown voltages obtained were higher than when the underlying metal was made negative. Both authors investigated the conductivity of the dry aluminium oxide films, and when D.C. was used demonstrated
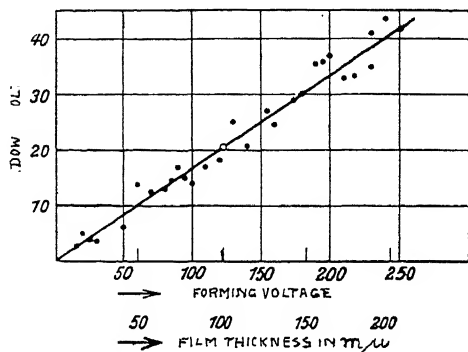
FIG. 90.—Breakdown Measurements on Tantalum Oxide Films (Tantalum as Anode) using Direct Voltages.
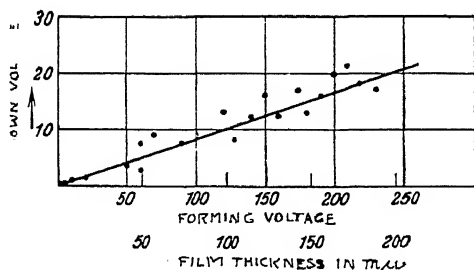
FIG. 91.—Breakdown Measurements on Tantalum Oxide Films (Tantalum as Cathode) using Direct Voltages.

that asymmetric values were obtained, whilst the phenomenon was not observed with A.C., either with moist or with dry films. The directional effect is, therefore, obviously very sluggish. Zauscher assumes that it is due to electrophoretic effects, whilst Holst attributes it to the migration of the hydroxyl and hydrogen ions in the film. These ions would be influenced by the strong electric field, the negative hydroxyl ions migrating towards the aluminium basis metal and giving rise to aluminium oxide, whilst the positive hydrogen ions migrate to the negative electrode and are evolved as hydrogen gas.

It hardly needs to be pointed out that moisture reduces the breakdown voltage of the oxide film.

An investigation carried out by Wöhr provides some interesting information on the influence of the frequency of the rectified A.C. used in the production of the oxide films on the breakdown voltage. He oxidized 99·5 per cent. aluminium sheet for 8 hours in 3 per cent. oxalic acid solution at 16° C., using D.C. of current density 1 amp./dm.², corresponding to a value of 1·23 amp./dm.² for the effective sinusoidal pulsating current. The breakdown voltage U_d measured between two flattened spheres each 50 mm. in diameter increased as the frequency of the forming current, which started
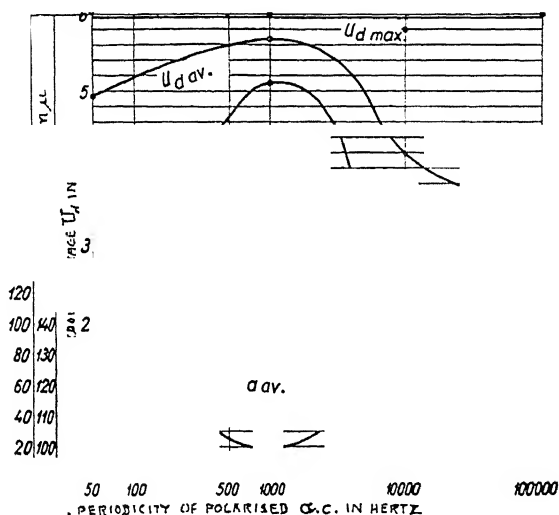
Fig. 92.—Breakdown Voltage and Thickness of Oxide Film in relation to the Periodicity during 8 hours' Treatment. U_d refers to oxide films on both sides of the sheet; a refers to oxide films on one side.

at 50 hertz, increased, to reach a maximum at about 1000 hertz, after which point it fell again rapidly. The relationship was influenced by the deviation S, so that it was necessary to make a large number of measurements and to give maximum $(U_{d\ max.})$ and minimum $(U_{d\ min.})$ values. Fig. 92 and Table XXVIII show the results obtained. The relative total deviation S corresponds to the expression :

$$S = \frac{U_{d\ max.} - U_{d\ min.}}{U_{d\ av.}} \times 100 \text{ per cent.}$$

According to Wöhr, the detachment of the anodic gas from the basis metal, that is to say, the diffusion of the electrolyte,

proceeded most effectively at a frequency of 1000 hertz. Greater periodicities than a few thousand hertz were wasted. The fact that the minimum deviation likewise occurs at 1000 hertz is the best proof of the uniformity and breakdown stability of the films produced at this periodicity. If it is considered that the average film thickness a is approximately equal over the whole range of frequencies investigated, it would appear that the observed variation of the breakdown voltage is due exclusively to the variations in structure of the film dependent on the frequency. It is of interest to note that the maximum value of about 6 kv. was obtained for the breakdown voltage at all the periodicities.

The dependence of the breakdown voltage on the time was investigated by Wöhr, who used test-pieces of aluminium wire 1·4 mm. in diameter provided with oxide films which were in one case untreated, and in the other case coated with bakelite. In the

TABLE XXVIII

Frequency of Rectified A.C., in hertz.	50.	1,000.	10,000.	100,000.
Single film thickness a in μ .	109	113·5	125	103
Breakdown voltage U_d of the double film in kv$_{\text{eff.}}$:				
average value $U_{d\ av.}$.	4·93	5·68	4·19	3·6
Maximum value $U_{d\ max.}$ . .	6·05	6·0	5·8	6·0
Minimum value $U_{d\ min.}$ . .	2·50	5·1	2·0	1·75
Relative total deviation S, per cent.	72·0	15·8	90·8	118·0

case of the untreated films, no relationship between the breakdown voltage and the time could be determined, but with the bakelite-coated films there was a slight but definite dependence on the time (within a range of 0 to 6 minutes, reckoned from the moment when the breakdown voltage began to operate).

Corrosion-resistance

The Reichsausschuss für Metallschutz (German National Committee for Protection of Metals) defines corrosion as the destruction of a metallic body produced by the undesired action of chemical attacking media on the surface of the body. Attack by which a desired change is induced in the metal surface by the application of properly controlled chemical or electrochemical processes does not, therefore, come under the definition of corrosion. Among such processes must be included etching, matt-etching, chemical and electrochemical oxidizing processes, and, finally, the processes of so-called metal coloration. Any undesired change in carrying out

these processes due to some error in the *modus operandi* again falls within the category of corrosion.

It has already been mentioned that the porosity of oxide films is a disadvantage in so far as their protective action against corrosive influences is concerned, but that this difficulty may be overcome by sealing the pores. If the pores are left open the film greedily absorbs liquids, which gain access to the metal and there bring about corrosion if the liquids in question have a corrosive tendency.

Zauscher has made a thorough investigation of the absorptive capacity for water of oxide films produced in 4 per cent. oxalic acid, both by A.C. and by D.C. The oxidized test-pieces were weighed after careful drying at 120° C., the values being corrected to relative humidity 0. The other humidity stages (33·5 to 80 per cent. relative humidity) were induced over calcium chloride solutions of known density in an exsiccator. The 100 per cent. humidity stage was arrived at by immersion in distilled water. In all the tests

TABLE XXIX

Test-piece.	Film thickness, μ.	Forming Current.	Impregnation.
L_1	10·8	D.C.	none
L_2	55·0	D.C.	none
L_3	7·8	A.C.	none
L_4	13·8	A.C.	none
L_5	20·8	A.C.	none
L_6	14·5	A.C.	linseed oil and wax
L_7	13·8	A.C.	bakelite C and wax

the temperature was maintained at 20° C. Table XXIX gives details of the film thickness, forming and impregnation of the films on the different test-pieces. Figs. 93-95 show the results which were obtained, the volume of water taken up after drying being expressed as a percentage of the volume of the film.

The curves show that thin films are more hygroscopic, and hence more porous, than thick films : and further, that films produced by A.C. take up more water than films produced by D.C.

The bakelite-coated film L_7 (the wax coating referred to in Table XXIX was volatilized on drying in the drying oven) gives a normal adsorption curve (Fig. 95), whilst with the unsealed films marked water sorption still occurs between 60 and 80 per cent. relative humidity. In contradistinction to the bakelite-coated test-piece, the test-piece L_6 impregnated with linseed oil and wax was found to be completely non-hygroscopic. No water was removed in the desiccator over phosphorus pentoxide, and it did not take up even traces of water at any stage of humidity.
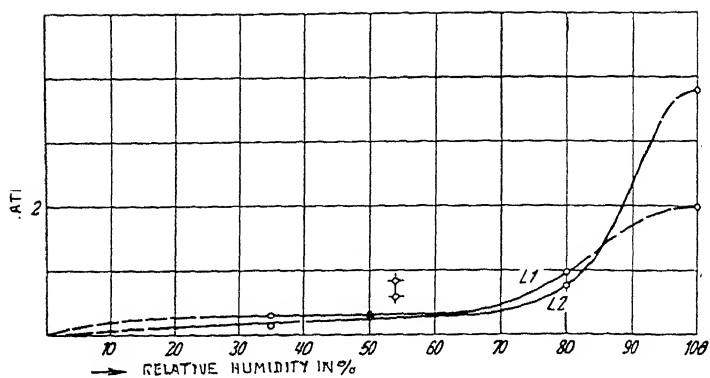
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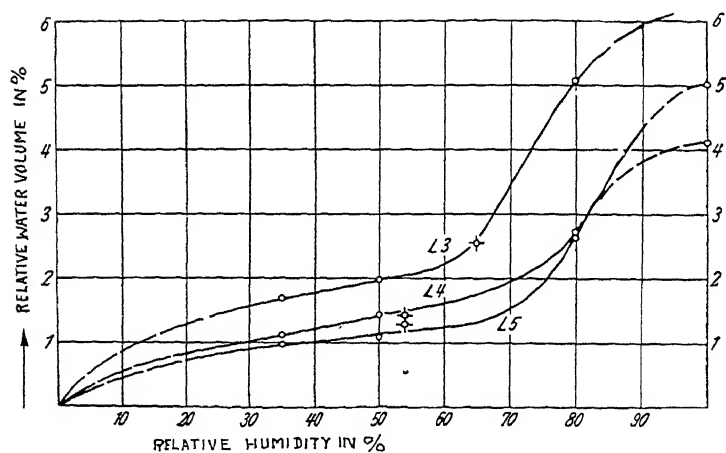FIG. 93.—Absorption of Water by D.C. Films.
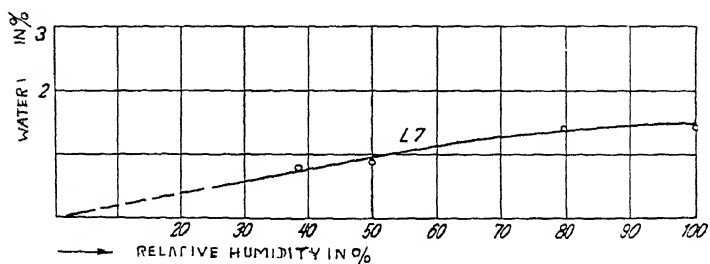

FIG. 94.—Absorption of Water by A.C. Films.

FIG. 95.—Absorption of Water by an Oxide Film impregnated with Bakelite.

Zauscher's researches show quite definitely the great tendency which the oxide films have to take up liquids and the possibility of counteracting this effect by simple methods. This is true not only of pure aluminium but also of alloys, more particularly the copper-containing alloys, which in themselves have little resistance to corrosion. By producing films on these alloys and sealing them by suitable methods, excellent corrosion protection can be obtained.

, Fig. 96[1] shows a number of duralumin test-pieces, with and without protective oxide films, which had been exposed for six months to the action of 10 per cent. common salt solution in the alternate immersion apparatus. The test-pieces D_1 and L_1, which were not oxidized, are strongly corroded, whilst all the other (oxidized)
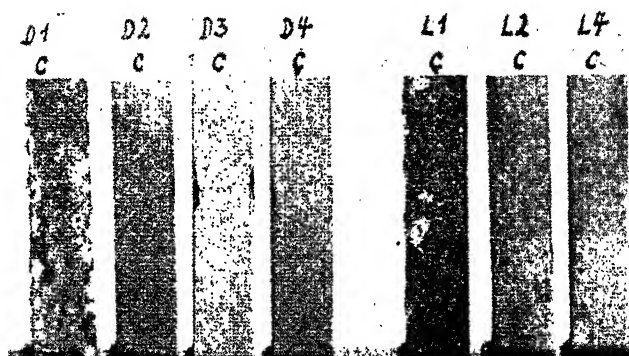
FIG. 96.—Protective Effect against Corrosion of Oxide Films on Duralumin Test-pieces. Test period of 6 months in 10 per cent. sodium chloride solution in alternate immersion apparatus. D_1 and L_1 are without protective films.

test-pieces show absolutely no sign of attack. (The dark marks on the edges are the lacquer which was used at the contact areas during the oxidation.) The heat-treated duralumin test-pieces which had been oxidized (L_2, L_4) also behaved satisfactorily. All the anodically oxidized test-pieces were sealed with linseed-oil varnish.

Fig. 97 shows graphically the results of tensile tests on oxidized duralumin sheet. The tests were carried out on test-pieces of the untreated alloy which had been exposed in the alternate immersion apparatus, for periods up to six months, to the action of 10 per cent. common salt solution. Both the ultimate tensile strength and the elongation had suffered badly in the case of the unprotected test-pieces. The oxide films produced in oxalic acid and in sulphuric acid gave practically equally good protection in the case of

[1] Researches by Messrs. Siemens & Halske A.-G.

duralumin, judged by the results of these tests.   The films were sealed with linseed-oil varnish.

When the testing was prolonged, however, a considerable difference in the corrosion behaviour was observed between the protective films produced by D.C. on duralumin in oxalic acid and in sulphuric acid respectively, as can be seen from the results shown in Table XXX and in Figs. 98 and 99.[1]   The duralumin test-pieces were oxidized by the processes ordinarily used commercially, in oxalic acid and in sulphuric acid.   The pores were sealed[2] in different ways (using linseed-oil varnish, water-glass, dichromate and hydrolysable heavy metal salts).   The treated test-pieces underwent corrosion testing in the alternate immersion apparatus, 10 per cent.
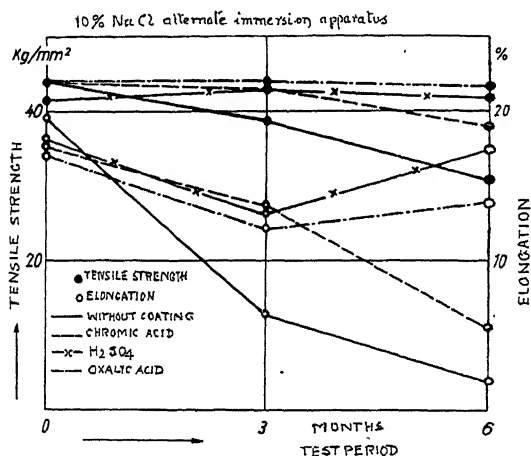
FIG. 97.—Tensile Strength and Elongation of Anodized Duralumin Sheets exposed for 6 months in an Alternate Immersion Corrosion-testing Apparatus.

salt solution being used.   The period of testing was prolonged for 2 years, during which test-pieces were withdrawn at certain time intervals for determinations of the ultimate tensile strength σ_B and the elongation δ.

These tests show quite clearly the superiority, so far as duralumin is concerned, of the films produced in sulphuric acid over those produced in oxalic acid in respect of their corrosion-resistance.

Whilst the films produced in sulphuric acid, with the exception of those sealed with water-glass, exhibited practically no change in tensile strength and elongation after the two years' period of testing, the oxalic acid films show a considerable reduction, more particularly in the case of the elongation.   Concordantly with these results the

[1] Researches by Messrs. Siemens & Halske A.-G.
[2] For details see pp. 165 and 204-206.

sulphuric acid films were completely unchanged in appearance after the two years' test period, whilst the oxalic acid films showed some areas of attack.
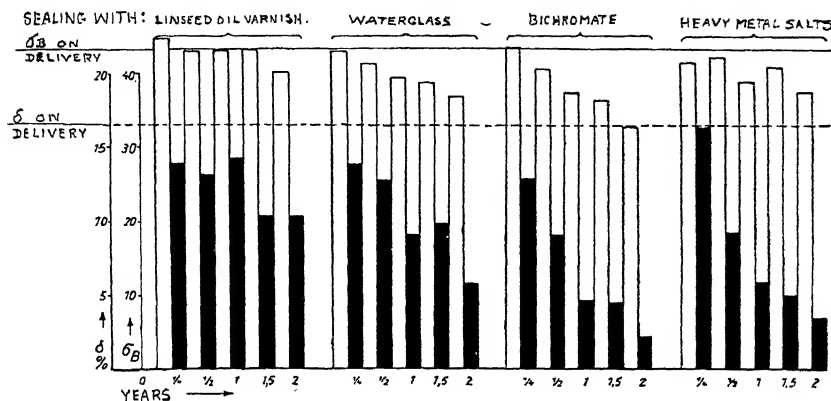
FIG. 98.—Tensile Strength (σ_B) and Breaking Elongation (δ) of Oxalic Acid D.C. Films on Duralumin during 2 years' Corrosion-testing in an Alternate Immersion Apparatus.
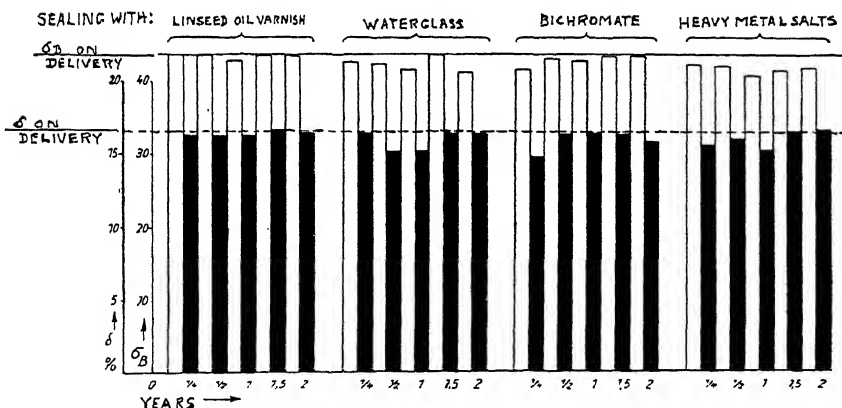
FIG. 99.—Tensile Strength (σ_B) and Breaking Elongation (δ) of Sulphuric Acid D.C Films on Duralumin during 2 years' Corrosion-testing in an Alternate Immersior Apparatus.

Corrosion-testing Methods

The best method of testing anodically oxidized light metal test-pieces for their corrosion-resistance is undoubtedly to expose them to the actual conditions which they have to withstand in practice : where it is intended to use anodized metal in the open air, corrosion tests should, therefore, embrace weathering tests either inland or

in sea air as well as corrosion tests in fresh water or sea water; also tests in tropical climates. The same applies to the determination of the corrosion-resistance in enclosed spaces in which smoke, steam or chemically active gases are commonly present. Since such tests

TABLE XXX.—CORROSION TESTING OF ANODIZED DURALUMIN

(σ_B = tensile strength, kg./mm.; δ = elongation, per cent.; 10 per cent. sodium chloride solution in alternate immersion apparatus.)

Process, i.e. Type of Film.	Pores Sealed with	As Supplied.		After 3 months.		After 6 months.	
		σ_B	δ	σ_B	δ	σ_B	δ
D.C., oxalic acid	Linseed-oil varnish	—	—	44·5	16·6	42·7	13·2
	Water-glass	—	—	43·0	13·9	41·2	12·8
	Dichromate	43·5	16·6	43·7	13·0	40·9	9·2
	Heavy metal salts	—	—	41·9	16·4	42·5	9·4
D.C., sulphuric acid	Linseed-oil varnish	—	—	43·5	16·2	43·4	16·2
	Water-glass	—	—	43·2	16·4	42·1	15·2
	Dichromate	43·5	16·6	41·8	14·8	43·1	16·4
	Heavy metal salts	—	—	42·1	15·6	42·0	16·0

Process and Type of Film.	Pores Sealed with	As Supplied.		After 1 year.		After 1½ years.		After 2 years.	
		σ_B	δ	σ_B	δ	σ_B	δ	σ_B	δ
D.C., oxalic acid	Linseed-oil varnish	—	—	43·0	14·5	43·1	10·8	40·1	10·8
	Water-glass	—	—	39·7	9·2	38·8	9·9	37·0	5·8
	Dichromate	43·5	16·6	37·7	4·8	36·5	4·6	33·0	2·5
	Heavy metal salts	—	—	39·6	6·0	41·2	5·1	37·9	3·6
D.C., sulphuric acid	Linseed-oil varnish	—	—	42·8	16·2	43·4	16·7	43·5	16·4
	Water-glass	—	—	41·6	15·3	43·5	16·5	41·1	12·2
	Dichromate	43·5	16·6	42·4	16·5	42·5	15·3	42·5	15·8
	Heavy metal salts	—	—	40·8	15·3	41·5	16·6	41·8	16·7

(Numbers in heavy type represent the mean of 3 measurements.)

take up very large amounts of time, attention has been directed to the development of rapid methods for laboratory use. These methods must, however, be considered as yielding only relative values, which are not capable of giving conclusive indications regarding the behaviour of a film under changed conditions.

Thus, it may, for example, appear from tests carried out on different films in normal hydrochloric acid (the volume of hydrogen evolved in a given time being measured) that one film behaves better than another. It is not possible, however, to conclude from this what will be the relative corrosion-resistance towards sea-water, even though we know that the attack of sea-water is considerably less vigorous than that of hydrochloric acid. The same applies to the accelerated test method frequently used in the laboratory, which depends on employing a common salt solution containing hydrogen peroxide. Both processes are suitable for drawing conclusions only when the factors for translating the results to the other conditions are known.

It is possible to arrive at a reliable result by determination of the loss of weight of an oxidized test-piece in a given corrosive medium only if solution takes place without any formation of insoluble corrosion products which adhere to the test-piece. If such products are formed, the weight may actually increase ; and this fact indicates corrosive attack, which is also evidenced by the outward appearance.

The most frequently used test methods in the laboratory at the present time are those employing the rotating liquid apparatus, the alternate immersion apparatus, and the salt spray apparatus. These methods use a 3, 5 or 10 per cent. sodium chloride solution, with or without the addition of 0·1 per cent. of hydrogen peroxide, as corrosive medium. In the rotating liquid apparatus the salt solution is kept in constant motion about the immersed test-pieces. Different arrangements are used for this test. In the alternate immersion apparatus the test-pieces under investigation are attached to a slowly rotating disc so that they are alternately immersed in the salt solution and dried in the air. The spray apparatus consists of a large chamber, appropriately constructed of glass, in which the test-pieces are hung and through which the salt solution is driven in the form of an extremely fine spray controlled by compressed air, so that the test-pieces are exposed to the simultaneous effect of air and salt water. The salt water mist takes several hours to settle in the apparatus, so that it is sufficient to introduce a fresh spray two or three times during the 24 hours. In a few cases corrosion tests may be carried out in stationary vessels : in this case the test-pieces are suspended motionless in the salt solution.

The test-pieces are removed from the apparatus as soon as the first visible attack, which frequently occurs at the cut edges, is seen. The period of test serves as a criterion of the quality of the film. At least five test-pieces provided with the same type of film should be used in the apparatus at the same time : the greater the number of test-pieces the more reliable is the average value obtained. Where more accurate investigations are being undertaken, the appearance

of the test-pieces is no longer sufficient criterion, and measurements are carried out to determine the variation in the tensile strength and elongation at certain time intervals during the test and at its conclusion (*cf.* Fig. 97). For these tests a larger number of test-pieces (20 and more) provided with each type of film are used. This method of corrosion testing is, therefore, time-consuming and costly.

Fig. 100 shows the results obtained in such an investigation in a stationary vessel. Tensile test-pieces of Silumin (13 per cent. Si),
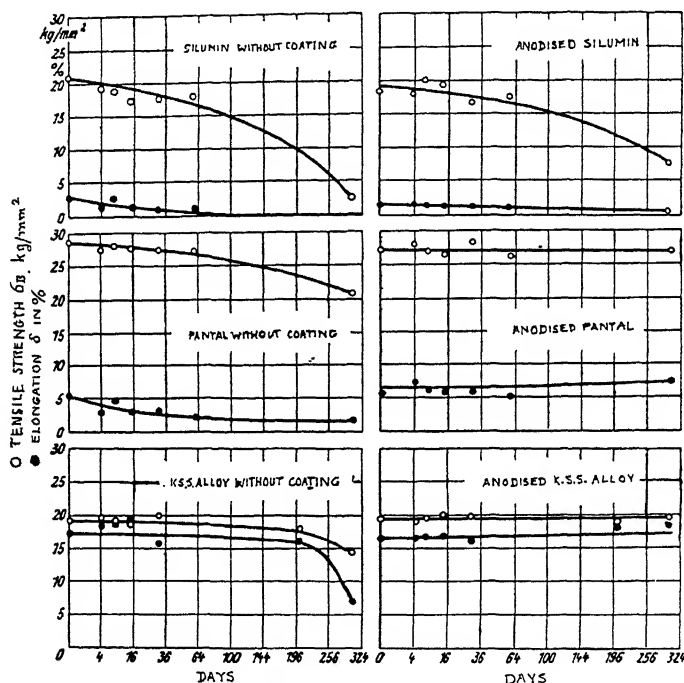
FIG. 100.—Corrosion-resistance of Electrolytically Produced Films on Different Aluminium Alloys in 3 per cent. Sodium Chloride Solution with 0·1 per cent. Addition of Hydrogen Peroxide Compared with Untreated Material.

Pantal (1·4 per cent. Mg, 0·9 per cent. Mn, 0·7 per cent. Si, 0-0·2 per cent. Ti) and KSS alloy (2 per cent. Mg, 1·4 per cent. Mn, 0·7 per cent. Si, 0·2 per cent. Sb), both in the untreated state and after anodizing, were given prolonged testing in a 3 per cent. sodium chloride solution to which had been added 0·1 per cent. of hydrogen peroxide and the tensile strength (in kg./mm.²) and elongation at fracture (per cent.) were measured at given time intervals.

Whilst in the case of Silumin and Pantal the test-pieces without a protective coating exhibited a rapid decrease both of tensile strength and of elongation, the decrease in the case of KSS alloy was slight

up to 196 days, but then progressed the more rapidly. In the case of the test-pieces provided with oxide films, only Silumin showed a marked falling off of the tensile strength, the elongation remaining unchanged. In the case of the anodized Pantal and KSS alloy test-pieces, both the tensile strength and the elongation were unaffected during the 10 months' period of test.

The foregoing observations indicate that there has hitherto been no uniform control of corrosion tests on light metals, so that it is impossible to make a direct comparison of the results of tests derived in different places. This gap is fortunately filled by the standard which has recently been issued by the Fachnormenausschuss für Korrosionsfragen (Technical Committee on Corrosion)[1], since it to a large extent meets the existing need for simple corrosion-testing methods which will give reproducible results ; results which, moreover, will be comparable with those obtained under service conditions. The specification contains details of the method of carrying out tests both under atmospheric conditions and in the laboratory. The extent of the corrosive attack is measured by tensile or other mechanical tests, and by observation of the changes which the surface undergoes and of the corrosion products ; finally, the attack is followed by means of metallographic investigations.

[1] *German Standards* D.I.N. E 4850 and D.I.N. E 4851.

CHAPTER IX

CHEMICAL PROCESSES AT THE ELECTRODES AND IN THE ELECTROLYTE

WE shall confine ourselves in the following to discussing those electrolytes which are of primary interest in the commercial production of protective films, *viz.* sulphuric acid, chromic acid and oxalic acid. These three acids represent different types, in so far as their behaviour at the electrodes is concerned. Sulphuric acid undergoes no change, either at the anode or at the cathode. Chromic acid remains unchanged at the anode, but at the cathode it undergoes reduction from the hexavalent to lower oxidation stages, and finally to metallic chromium. Oxalic acid is subject to extensive changes at both electrodes, being reduced at the cathode and oxidized at the anode.

All three acids possess the common property of having some solvent effect on the film once formed or on the aluminium. In all cases, therefore, the acid is used up, due to neutralization, and the bath becomes exhausted, which fact evidences itself in its diminishing effectiveness. In commercial practice, where plants are run continuously for long periods and with a full load, it is accordingly necessary to institute proper supervision of the composition of the bath.

We have already discussed in some detail the changes which occur at the electrodes, more particularly at the aluminium anode. It has been shown that the cathode does not change if it consists of a material which is inert towards the electrolyte. If aluminium is to be used as the cathode there are no difficulties, provided the electrolyte is kept cool, since the slight attack which the cold electrolyte exerts rapidly comes to a standstill, as has been shown earlier, and is to all intents and purposes unimportant.

There are still some facts to consider regarding the chemical processes at the anode. Analysis of the gases formed at the aluminium anode during electrolysis in oxalic acid shows the following composition : 76·6 per cent. oxygen, 16·4 per cent. carbon dioxide, 7·0 per cent. hydrogen. W. Beetz has found that hydrogen occurs at the anode in sulphuric acid only when high current densities are used : it can arise only from a direct action of the acid on the metal. This is a proof of the fact that the electrolyte can in certain circumstances, even during electrolysis, penetrate

through the pores of the film to the anode. The carbon dioxide is the oxidation product of the oxalic acid. Since the oxygen which evolves as gas accounts for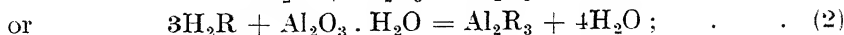 only some 4 to 5 per cent. of the oxygen discharged at the anode, that is to say, since only 95 to 96 per cent. of the latter is actually used in the oxidation of the aluminium, oxygen is invariably present in excess in its most active (atomic) form.

If we consider the discharge potential[1] of the SO_4'' ion ($-1 \cdot 9$ v.) and of the O'' ion ($+1 \cdot 23$ v.) it follows that on electrolysis in sulphuric acid the O'' ion,[2] which is always present, is preferentially discharged before the SO_4'' ion with its higher potential. The oxygen combines, in the extremely active form in which the O'' ion exists immediately after being discharged, with the also highly active aluminium to form Al_2O_3 directly. Since the reaction is taking place in an aqueous medium, water can take part in the decomposition; so that according to the particular conditions the aluminium oxide which is formed may be more or less hydrated. It has not been observed with any degree of certainty that the highest stage of hydration, namely that in which the aluminium hydroxide is in the form of a gel, occurs at any stage of the reaction. The conjectures frequently made in the literature that the aluminium salt primarily formed at the anode is precipitated as a result of hydrolysis as $Al(OH)_3$, which migrates electrophoretically to the anode, there to be dehydrated, do not take account of the conditions which actually obtain at the anode. It is improbable that the reaction of the strongly acid electrolyte attains the neutral point in the neighbourhood of the anode, so that hydrolysis is most unlikely to occur. In any case, the positively charged hydroxide which would be formed from an aluminium salt solution can certainly not migrate to the anode.

These considerations show in a perfectly definite way that the film formation is purely a phenomenon of direct oxidation, in connection with which it is superfluous to assume intermediate stages. The course of the reaction may accordingly, depending on the conditions of oxidation, be formulated as follows :

$$2Al + 3O = Al_2O_3;$$
or
$$2Al + 3O + H_2O = Al_2O_3 . H_2O, \quad \quad \quad (1)$$
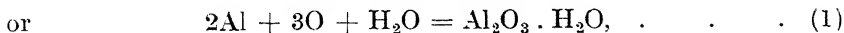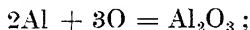
the water content varying between the two limiting values of 0 and about 15 per cent. The film formed and/or the aluminium then dissolves in the dibasic acid, H_2R, in accordance with the equations :

$$3H_2R + Al_2O_3 = Al_2R_3 + 3H_2O;$$
or
$$3H_2R + Al_2O_3 . H_2O = Al_2R_3 + 4H_2O; \quad \quad (2)$$
and
$$3H_2R + 2Al = Al_2R_3 + 3H_2. \quad \quad (3)$$

[1] See Tables IV and V, p. 25.   [2] *Cf.* p. 12.

Of the two processes shown by equations (2) and (3), solution takes place predominantly in accordance with equation (2), at least in the equilibrium state, where a balance is maintained between the formation of the film and its destruction; whilst solution of the metal, which takes place in accordance with equation (3), is of subordinate importance under the operating conditions which are usual in the commercial production of protective films.

The anodic oxidation of oxalic acid goes to completion in accordance with the equation :

$$C_2O_4H_2 + O = 2CO_2 + H_2O. \qquad . \qquad . \quad (4)$$
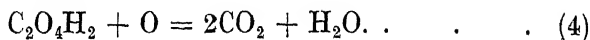
This oxidation does not occur with sulphuric acid or chromic acid electrolytes, so that the quantity of oxygen here involved is available for the formation of the film.

It must be assumed that the reaction of the oxalic acid at the cathode involves the whole series of reduction products derived from oxalic acid, thus :
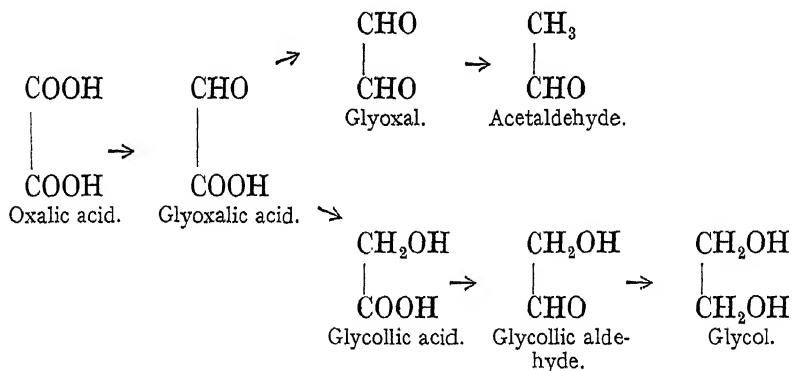
Qualitative tests on an oxalic acid solution about 3 per cent. in strength used for the oxidation of aluminium showed the presence of glyoxalic acid and acetaldehyde, but it was not possible to detect their presence in very dilute 0·35 per cent. oxalic acid solution. Analyses of oxalic acid solutions which had been used for a long time in the oxidation plant of Messrs. Siemens & Halske A.-G. demonstrated in one case the presence, in addition to glyoxalic acid, of a trace of glycollic acid. The glyoxalic acid was isolated quantitatively as the calcium salt ; its content in one of the baths was found to be 0·18 g./100 cc.

CHAPTER X

SUPERVISION OF THE BATH

Exhaustion and Replenishment of Oxalic Acid Baths

THE consumption of the oxalic. acid is due to the following :

(1) Dissolution of the film.
(2) Dissolution of the aluminium. $\Big\}$ Loss due to neutralization.
(3) Reduction of the oxalic acid at the cathode.
(4) Oxidation of the oxalic acid at the anode. $\Bigg\}$ Loss due to processes at electrodes.

In the case of chromic acid the first three processes occur, but in the case of sulphuric acid only the first two come into consideration.

An additional source of loss, which has to be reckoned with in the case of all baths, is the quantity of liquid which adheres to the surface of the objects treated and which is removed with them when they are taken from the bath. The loss on this score is of subordinate importance ; it can readily be noted simply by measuring the depth of the liquid in the bath, and once it has attained a certain degree fresh liquid can be added to fill the bath to the original level.

The losses due to neutralization and to the processes at the electrodes are determined by titration and if necessary by simple calculation if the titrimetry is indirect. Fig. 101 indicates in a simple fashion the conditions which obtain. It relates to a bath containing freshly prepared 5 per cent. oxalic acid. After continued use for oxidation, the solution is titrated against caustic soda, which indicates a content of free acid equal to f per cent., and then with potassium permanganate, which indicates a total oxalic acid content of g per cent., this value including both the free acid and the combined acid which has taken part in the solution of the

FIG. 101.
Diagram representing Consumption of Oxalic Acid.

aluminium and/or aluminium oxide.[1]   Expressing all the values as weight per cent. per unit volume, *i.e.* as g./100 cc., we have, therefore :

Content of freshly prepared bath   . $= 5$;
Total acid by titration   .   .   . $= g$;
Free acid by titration[2]   .   .   . $= f$;
Loss due to processes at electrodes   . $= 5 - g = y$;
Loss due to neutralization .   .   .. $= g - f = x$;
Total loss of acid (*i.e.* amount requiring
    to be added) .   .   .   .   . $= 5 - f = x + y$.

From the quantity of acid x combined with the aluminium, the aluminium content of the bath may be calculated, since in the molecule of aluminium oxalate, $Al_2(C_2O_4)_3$, there are three molecules of oxalic acid ($3 \times 90 = 270$) to two atoms of aluminium ($2 \times 27 = 54$) : *i.e.* 270 g. of oxalic acid are neutralized by 54 g. of aluminium,
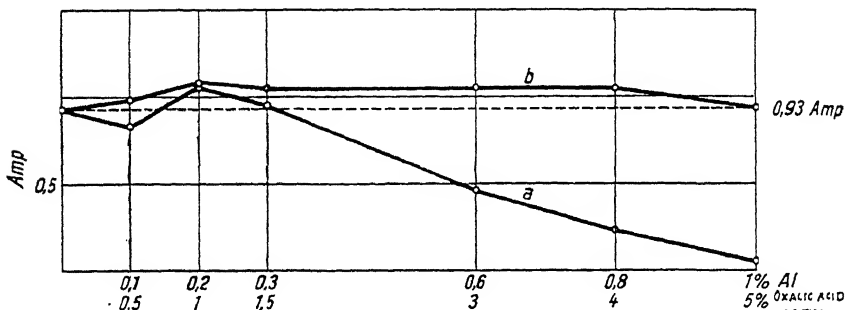
or 1 g. of oxalic acid is neutralized by 0·2 g. of aluminium.   If the loss due to neutralization be x per cent. the quantity of aluminium in solution is, therefore, $0·2 \times x$ per cent.   In practice it has been found by experiment that a hot aqueous solution containing 5 per cent. of anhydrous crystalline oxalic acid does not dissolve more than 1 per cent. of aluminium.   The aluminium content of the bath can, of course, also be determined gravimetrically.

    Curve *a* in Fig. 102[3] and Table XXXI give information regarding the influence of the aluminium content of a solution (which originally

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[1] No account is taken here of the small quantities of glyoxalic acid or other reduction products which occur in traces as a result of processes at the cathode ; these can be neglected without introducing any appreciable error in a works analysis of the type described.   The carbon dioxide which is set free at the anode is for the most part liberated into the air.

[2] The estimation of the free oxalic acid may be quickly and conveniently carried out with the help of colorimetric methods, according to researches by Messrs. Siemens & Halske A.-G.

[3] Researches by Messrs. Siemens & Halske A.-G.

contained 5 per cent. of crystalline anhydrous oxalic acid) on the current and on the growth in thickness of the film. The investigations were carried out in the following manner : from a large quantity of an oxalic acid solution of the above-mentioned concentration freshly made with distilled water, seven portions, each of 3 litres, were taken, and increasing quantities of aluminium foil (0·1, 0·2, 0·3, 0·6, 0·8 and 1 per cent.) were dissolved in the respective portions. Keeping the terminal voltage constant at 60 v. and using an aluminium anode of 0·5 dm.² surface, the average current during one hour's oxidation in the freshly prepared solution at 20° C. was found to be 0·3 amp., whilst the film thickness attained 41·2 μ. As the aluminium content increased, the average current steadily decreased (if we except the somewhat higher values obtained in

TABLE XXXI.[1]--EXHAUSTION AND REPLENISHMENT OF OXALIC ACID.

(Solution originally contained 5 per cent. $C_2O_4H_2$; bath operated at 20° C. and 60 v. for one hour ; anode surface = 0·5 dm.²)

Aluminium, per cent.	Mean Current, amp.	Film Thickness, μ	Oxalic Acid Added, per cent.	Mean Current, amp.	Film Thickness, μ
0·0	0·93	41·2	—	—	—
0·1	0·83	35·3	0·5	0·98	44·1
0·2	1·05	30·9	1·0	1·08	38·2
0·3	0·95	26·5	1·5	1·05	38·2
0·4	0·46	20·6	3·0	1·05	44·1
0·5	0·24	14·7	4·0	1·04	44·1
0·6	0·06	approx. 2·9	5·0	0·93	50·0

the case of the 0·2 and 0·3 per cent. aluminium contents) to reach a value of about 0·06 amp. at the point of saturation with aluminium (1 per cent.). The film thickness correspondingly decreased, as was shown by microscopic measurements. The final value of 2·9 μ in the third column of the table is estimated, the film being so thin that interference colours could be observed.

Curve b and the corresponding values for the film thickness in column 6 of the table show that the current, and hence the growth in thickness of the film, remain practically unchanged if the content of 5 per cent. of free acid is maintained by replenishing the oxalic acid used up by neutralization.

The question now arises as to how often replenishment of the exhausted oxalic acid should be made so that there is no serious interference with the current and with the growth in thickness, if the remaining operating conditions of oxidation (voltage, bath

[1] Researches by Messrs. Siemens & Halske A.-G.

temperature, period of treatment) are kept constant. Fig. 103[1] gives some interesting information on this point. After the bath had been for the first time completely exhausted by the dissolution of 1 per cent. of aluminium, and had had a corresponding addition of fresh acid (5 per cent. $C_2O_4H_2$) to replenish that combined with the aluminium, the initial average current (0·93 amp.) and hence the initial growth of the film were re-attained. After the further dissolution of 1 per cent. of aluminium foil had occurred the current and growth in thickness again decreased. The bath now contained 10 per cent. of $C_2O_4H_2$ and 2 per cent. of aluminium. When fresh oxalic acid was gradually added the current again rose, and when the addition had reached 5 per cent. of $C_2O_4H_2$ the average current
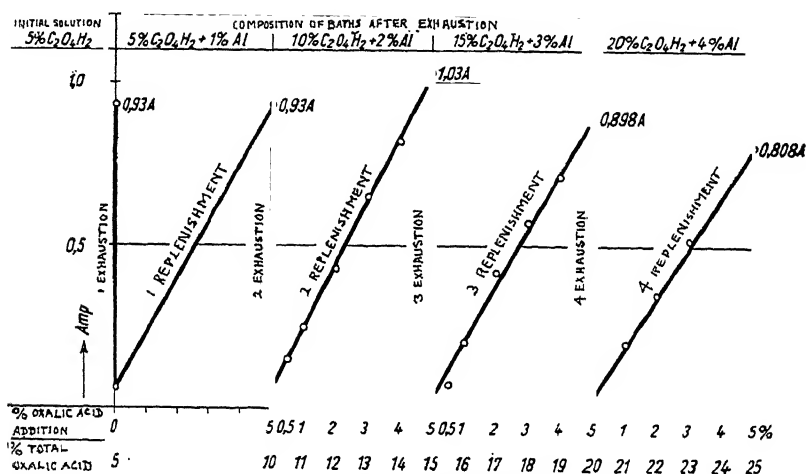
Fig. 103.—Repeated Exhaustion and Replenishment of Oxalic Acid Baths.

was 1·03 amp. Proceeding in this way with the exhaustion and replenishment of the bath, the steepness of the linear rise in current fell off markedly during the third and fourth replenishments, and after the fourth the average current during the one-hour's treatment was only 0·808 amp. It follows from this that the growth in thickness of the film under the given conditions of oxidation markedly decreased, even when the content of free acid was maintained, once the aluminium content exceeded 3 per cent. Only by raising the voltage or prolonging the duration of oxidation was it possible to obtain films of the original thickness. In routine processing neither of these alternatives is practicable, and such a bath has, therefore, to be regarded as finally exhausted.

Tests over a long period and the operation under works conditions of a bath have shown, in good agreement, that a freshly prepared

5 per cent. oxalic acid bath may be considered to have a life of 2 to 3 months provided the acid used up is regularly replenished and the ordinary loading of the bath of 1 m.²/500 litres is observed.

Exhaustion and Replenishment of Sulphuric Acid Baths

With the sulphuric acid electrolyte conditions are exactly similar. In this case also the current falls off as the aluminium content increases, when the voltage is kept constant at 15 v. The initial solution used contained 15 per cent. by volume of chemically pure sulphuric acid (sp. gr. 1·83); the temperature was maintained at 18° to 21° C., and aluminium sheet of 1 dm.² surface was used as anode. Fig. 104 and Table XXXII show that the mean current
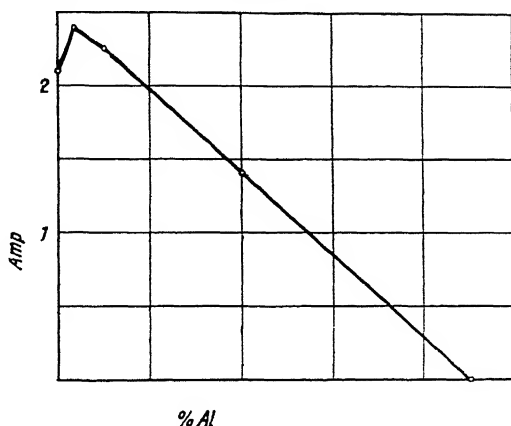
FIG. 104.—Falling off of Current in Sulphuric Acid with Increasing Aluminium Content.

density and hence the film thickness fall off as the aluminium content increases.[1] There is also an exception in this case, which occurs with 0·2 and 0·5 per cent. of aluminium, where a slight rise was noted with a corresponding increase in thickness of the film (cf. Table XXXII).

TABLE XXXII
Constant voltage 15 v.

Aluminium Content, g./100 cc.	Mean C.D., amp./dm.²	Film Thickness, μ.
0	2·1	26·0
0·2	2·45	28·8
0·5	2·25	26·6
2·0	1·35	17·6
4·64	not readable	—

[1] Researches by Messrs. Siemens & Halske A.-G.

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If the neutralized sulphuric acid is replenished by the addition of fresh acid, the current density and growth in thickness remain practically constant, as can be seen from Table XXXIII.

If the aluminium content reaches 2 per cent. (2 g./100 cc.) the current density at 15 v. falls to 1·35 amp./dm.², whilst in aluminium-free solutions it is 2·1 amp./dm.² When the acid is subsequently replenished, a crystalline precipitate of a difficultly soluble aluminium sulphate is formed, and this makes the electrolyte very cloudy. In this bath, even when the voltage was raised to 20, the current was found to be only 0·5 amp. Hence, it must be taken that the sulphuric acid electrolyte cannot be further replenished after the aluminium content has risen to 2 per cent. Exhaustion of the bath is indicated by the cloudiness due to the crystalline precipitate, and by the falling current density and rising voltage.

TABLE XXXIII

Constant voltage 15 v.

Aluminium Content, g./100 cc.	Sulphuric Acid (sp. gr. 1.83) Added, cc.	Mean C.D., amp./dm.²	Film Thickness, μ.
0·2	—	2·45	28·8
—	25·82	2·35	27·2
0·2	—	2·35	28·8
—	25·82	2·53	32·8
0·2	—	2·15	26·3
—	25·82	2·16	28·0

The free sulphuric acid was determined in the above tests in the ordinary way by titrating a sample from the bath against caustic alkali.

Impurities in the Bath : Prevention and Removal

Amongst the impurities in the bath, the aluminium which is present due to direct solution of the metal or of the oxide film in the bath liquid, which has been referred to in the preceding paragraphs, is the most important. In addition to this major impurity of aluminium there may be present other substances derived from the constituents in the aluminium alloys, such as copper, magnesium, manganese, silicon, and sometimes also zinc.

No cases of difficulty due to dissolved magnesium or zinc have been known up to the present. Copper goes partly into solution, and if copper-containing alloys are given prolonged oxidation the electrolyte becomes coloured bluish or greenish. To some extent, the copper is deposited cathodically in a spongy, pulverulent form ; it sinks from the cathode to the bottom of the bath, or else it may

be dispersed in a flocculent form in the moving liquid. So far as the author's knowledge goes, this presence of copper does not interfere with the oxidation process ; at least, he is aware of no such interference. Nevertheless, it is desirable to remove the copper deposit from time to time by cleaning the cathode and to remove it from the bath by decantation or filtration, since, in order properly to supervise the bath, the liquid should always be kept clear. If filtration is undertaken it should be carried out by means of a device fitted with a pump.

If Silumin is treated for a long time in the oxidation bath, the electrolyte soon becomes cloudy and brownish. The finely divided silicon suspended in the liquid can give rise to disturbances of a serious nature[1] and must, therefore, be removed from time to time by filtration. It has been observed that the silicon settles in the form of a grey deposit on the oxidized parts, and this deposit must subsequently be removed by brushing. In oxalic acid baths operated at high temperature and voltage with the object of obtaining light, almost colourless films (GXh process, *vide infra*), the presence of finely divided silicon in the liquid may completely prevent the formation of the light-coloured film. Certain observations also lead to the belief that in many cases pitting on anodized objects is due to the presence of silicon as impurity in the oxalic acid baths. Here again, therefore, it is essential to observe the rule that the bath liquid should be kept clear.

The presence of grease or oil in the bath is most objectionable. When the objects are removed from the bath any grease which may be floating on the surface of the liquid is taken up by the film, from which it cannot subsequently be completely removed. The grease or oil forms an emulsion with the water which the film has absorbed, and this makes itself unpleasantly obvious in the form of whitish specks. The presence of grease in the film interferes seriously with the sealing of the pores or the dyeing of the film, since neither the aqueous sealing material nor the dye is taken up at the greasy areas. In such cases there is no alternative other than to remove the film by pickling and to repeat the anodizing. What has been said also applies to touching anodized objects, which have not yet been sealed, with dirty or greasy fingers ; these invariably leave behind visible fingerprints which, in the majority of cases, cannot be removed.

In order to prevent contamination of the bath by greasy or oily substances, it is essential, in addition to observing general cleanliness, to ensure : (1) that the objects to be anodized are thoroughly degreased ; (2) that the air used to keep the bath in movement is filtered. The degreased objects, which have been pickled in caustic soda, should preferably be neutralized in dilute

[1] According to researches by Messrs. Siemens & Halske A.-G.

nitric acid and must be thoroughly washed in running water before they are introduced into the bath.

Special attention must be paid to the presence of chlorine ions in oxalic acid baths. Minute quantities of sodium chloride or hydrochloric acid can render the bath completely unusable. When the bath is prepared, therefore, it is essential to employ only distilled water or clean condenser water which is free from grease, and it is only permissible to use tap-water if this is free from any detectable quantity of chlorine. The upper limit of the permissible chlorine content in oxalic acid baths is for pure aluminium[1] 40 mg./litre and for duralumin[2] it is 20 mg./litre. If these limits are exceeded, pitting occurs over the whole of the metal surface, which has a rough feeling and appears matt. In contrast to what occurs with oxalic acid electrolytes, no deleterious effect is observed with sulphuric acid baths up to a chlorine content of 3000 mg./litre (0·3 per cent. Cl), so that tap-water may be used for the preparation of these baths. It is, nevertheless, desirable when replenishing the bath to use only water free from detectable chlorine, so that enrichment of chlorine cannot occur.

It is not necessary to stress the fact that, apart from the impurities we have referred to, care should be taken that no other impurities gain access to the bath, and that the utmost cleanliness is observed.

[1] Researches by Messrs. Siemens & Halske A.-G.   .

[2] The concentration of 40 mg. of chlorine per litre applies to the warm (35° C.) bath used for pure aluminium. Where an oxalic acid bath is being operated at 18° to 20° C. a higher chlorine content of the order of 110 mg./litre is not objectionable for aluminium. In the case of duralumin the upper limit permissible with both baths is 20 mg. of chlorine per litre. According to researches by Messrs. Siemens & Halske A.-G.

CHAPTER XI

CONDITION OF THE MATERIAL AND SHAPE OF THE OBJECTS AS CAUSES OF FLAWS IN THE FILM

WE have discussed in previous paragraphs the influence which the chemical composition of the metal has on the growth of the film and on the intrinsic colour of the film. We shall show in the following how the condition of the surface, the type of structure and the form or shape of the objects to be treated may be responsible for flaws in the film.

Influence of the Nature of the Surface

The first condition for a smooth-surfaced film free from flaws is a correspondingly smooth metal surface. Any cuts, scratches or similar irregularities are not covered up by the film, but remain quite visible even after oxidation ; in fact, in many cases such flaws show up more clearly after oxidation than they did on the material beforehand. This is true both of castings and of forgings. In the case of the former, there is also the possibility of the existence of pores and blowholes, which represent a serious difficulty in the way of producing good films whose protective effect is not to suffer. A non-porous, smooth, cast surface is the basic condition for the production of an effective protective coating and a film free from flaws.

Whilst scores and other surface markings may be removed by grinding and polishing, these means are not adequate to prepare a porous casting which suffers from blowholes in a suitable state for anodizing. Any foreign bodies or impurities present in the metal surface may interfere with the formation of a uniform film and may in many cases even produce pitting. Such foreign bodies or inclusions may be introduced by mechanical working processes, such as rolling, drawing, extrusion, etc., or by casting, and they may be of either metallic or non-metallic nature. The presence of heavy metal flecks in rolled material, of iron turnings in material which has been worked with machining tools, or of grains of sand in the case of sand-castings may, *inter alia*, be observed. In the case of many alloys, any particles of iron remaining in the surface may give rise

to serious consequences.   Fig. 105 shows how corrosion has occurred at the worked areas, the edges and the threads of Hydronalium castings.[1]   On examination it was possible to show the presence of a brownish inclusion at one of these areas ; and when this was analysed microchemically it was found to give a strong reaction for iron.

Influence of the Structure

It frequently occurs that a surface which appears homogeneous exhibits irregularities after anodizing.   This may arise in the case of
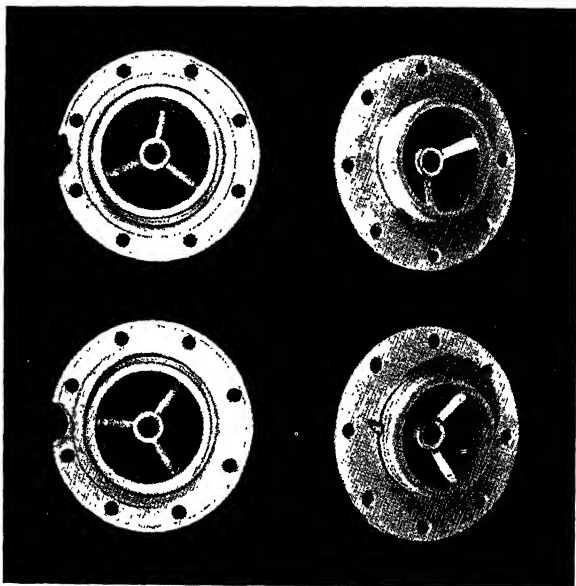
FIG. 105.—Corrosion at Worked Parts of a Hydronalium Casting.

both forged and cast material, either with pure aluminium or with alloys.   Aluminium sheet polished from the rolls, and apparently free from flaws, may, after anodizing, present a streaky or honeycombed appearance ; and the same phenomenon may be observed in the case of forging alloys, added to which a discoloration arising from the alloying constituents may be present.   In both cases, heterogeneity of the structure, which is in many cases attributable to zonal segregation or coring of the alloying constituents, is the cause.   Matters may be improved in many cases by suitable heat-treatment followed by quenching, which gives rise to a homogeneous,

[1] Researches by Messrs. Siemens & Halske A.-G.

fine-grained structure, which imparts to the protective films a uniform appearance. This may frequently be carried out successfully with extrusions.

In many casting alloys, for example Hydronalium, the tendency to form a coarse-grained heterogeneous crystal structure is very strong ; and it is impossible to produce a uniform film on these coarse-grained Hydronalium castings. In the majority of cases, however, by suitable heat-treatment followed by quenching it is possible to arrive at a fine grain, and consequently to produce a satisfactory film. The aluminium-magnesium-zinc alloy G 54 has given excellent results. The alloy has good casting properties, the castings produced being of fine-grained structure and almost free from pores. As a result it is possible to produce silver-white, uniform protective films on this alloy.

It is of great importance in the commercial production of protective films, accordingly, to use only tested alloys which have proved satisfactory. In the case of castings, it is essential that detailed attention should have been paid to all the aspects of casting technique, and in all cases it is important to produce a uniform, fine-grained crystal structure by suitable heat-treatment. Since sand-castings frequently have inclusions of sand from the mould, and moreover possess a coarser crystalline grain and a rougher surface than die-castings, the latter are in general preferable for treatment by anodic oxidation, unless preliminary mechanical finishing, such as grinding and polishing or matt-surfacing, can render the former fit for use.

It should be borne in mind that the positions at which gates have been used in the casting, which are not visible before treatment, frequently become so on anodizing, due to the differences in the crystalline structure at the areas in question and in the surrounding metal.

Throwing Power of Anodic Oxidation Baths

The conception of throwing power is familiar from electroplating procedure. The throwing power of a plating bath is said to be good if the formation of a metallic deposit is substantially independent of the distance of the different parts of the object under treatment from the anode. For example, a bath possesses good throwing power if, when a bowl is suspended in the electrolyte with the plane of its open top parallel to the two anodes, a metallic coating which, without being of absolutely uniform thickness, at least presents everywhere a uniform appearance, is produced both on the convex and on the concave surfaces. If this is not the case the throwing power is adjudged bad. Since in the case of electroplating the deposit is metallic and a good conductor, the resistance of the

electrolyte determines the current density at the different parts of an object, so that those parts close to the anode are exposed to a heavier current density and accordingly receive a thicker deposit than the areas further removed.

The conditions are quite otherwise in the case of anodic oxidation, in which the resistance of the electrolyte is in general extremely small in comparison with that of the anodically forming film. A bowl suspended in an anodizing bath with the plane of its opening parallel to and between two cathodes is, accordingly, coated with a film which is virtually uniform in thickness at all points. Even an aluminium sheet hung parallel and close to a single cathode will be covered on both sides with a film. As soon as the resistance of the electrolyte between the cathode and the face of the sheet nearest to it, plus the resistance of the film formed on this side, become equal to the resistance of the electrolyte between the cathode and the side of the sheet away from the cathode, film formation begins on the latter. Hence, the throwing power is very good in the anodizing process, and it follows that bowls, beakers and other hollow bodies with wide openings may be provided with a uniform film over the whole surface without necessitating the use of an auxiliary cathode. It is necessary to use an auxiliary cathode only if the objects for anodizing are in the form of hollow bodies with comparatively narrow openings, in which case the resistance of the electrolyte inside the hollow space increases considerably as a consequence of the narrow cross-section of the column of fluid reaching the interior.

Influence of the Shape

The shape of the objects to be treated in many cases determines the type of current connections which must be employed and the position which must be assigned to the objects when they are suspended in the electrolyte.

In the case of wire—to treat which, baths several metres in length are as a rule required—it is desirable to approach the current-bearing guide roll close to the surface of the electrolyte. The longer the bath the quicker the wires can be passed through, and the greater the output. It must be remembered that the cross-section of the wire which cuts the surface of the bath is the area of maximum current density, since the wire possesses no film at the moment of its entry into the electrolyte. Hence, at this point high temperatures occur and in the majority of cases sparks are observed. As the wire is passed through the bath, the film thickness increases and the current density decreases progressively between the point of entry into the bath and the point at which the wire emerges.

When hollow bodies are being anodized the contact clamps

should be arranged in such a way that the opening of the body is directed upwards, in order to allow any gases to escape freely. Care must also be taken to allow any gases evolved at the under face of the object to escape, and for this reason it is desirable to have the plane of the opening of a beaker, bowl, etc., inclined at about 45° to the horizontal. In the case of more complicated shapes, it is frequently difficult to arrive at a suitable position, and it may be necessary to stop anodizing for a brief interval and turn the object into another position, so as to produce an anodic film of the greatest possible uniformity over the whole of the surface. Such cases are, however, rare. If care is not taken to suspend hollow objects in the correct position, so-called air or gas pockets may be formed, preventing access of the electrolyte to the metal; so that film formation stops at these areas and a considerable rise in temperature may occur, which may often lead to eating away of the metal.

The anodizing of churns, cans or tubes, where it is desired to produce a film on the interior walls, presents greater difficulties. In this case the throwing power of the anodizing bath[1] is no longer adequate, and it becomes necessary to use an auxiliary cathode. This should preferably be an aluminium or copper wire of suitable thickness, on which an insulating material, such as glass beads, Pertinax discs, etc., is threaded in order to prevent short-circuiting with the anodically polarized object under treatment. Provision must also be made for the cooling of the electrolyte inside the hollow body. This can be arranged by allowing the electrolyte, maintained at the proper temperature, to flow through the hollow part, either by feeding it from a suitable height or by pumping it. By using such an arrangement it is possible to produce protective films on the interior surfaces of tubes several metres in length.

Various difficulties are presented by the anodizing of objects with flanged edges. In the first place, the flanges produce very narrow hollow areas only a few millimetres in diameter, for the anodizing of which there is no question of finding a suitable position of suspension in the electrolyte, of using an auxiliary cathode or of providing for cooling in the inside of the hollow. As a consequence, there is always a certain risk, when treating such objects, of the formation of air pockets and of local heating, which in turn lead to eating away of the metal. A second difficulty consists in the fact that when the anodizing treatment is finished it is not easy completely to remove the electrolyte from the flange; even continued rinsing is in many cases ineffective, and if even traces of sulphuric acid remain within the flange the metal will ultimately be attacked, white patches being formed at the edge of the opening of the flange. The film is in most cases destroyed at such areas, as is evidenced when dyeing of the film is tried, the dyestuff not being taken up at

[1] *Cf.* pp. 183-184.

these points. This difficulty can be removed by washing out the electrolyte *in vacuo*. Where the electrolyte is oxalic acid, this risk of the film being destroyed and of the formation of patches does not arise.

Flanges with steel or brass wire inserts must be regarded as completely unsuitable for treatment. With such flanges there nearly invariably arise corrosion areas, since the current, once it finds a high resistance in the initially formed aluminium oxide film, chooses to pass entirely through the steel or brass ; and the high current densities which arise in these metals produce considerable heating effects, with all their disadvantages. Accordingly, objects flanged with heavy metal inserts are quite unsuited for anodic oxidation.

Pores and blowholes in castings may, in some circumstances, give rise to the same effects as certain hollow bodies, for gas may collect in them and block the entry of the electrolyte. This means that a film cannot form in the pores, and hence the desired protective effect is lost. For this reason as well it is necessary to emphasize that good castings, free from pores and blowholes, must be employed.

Objects Made up of Several Parts

Where objects are made up of several parts joined by rivets or welds, it is in general necessary to ensure that the same material is used for all the components in order to exclude the possibility of the formation of local elements. Nevertheless, it is unavoidable in some cases, for reasons of design, to prevent the attachment of heavy metal components to objects of aluminium or aluminium alloys.

If objects consisting of several parts of the same nature are to be anodized, the precautions which have been referred to in connection with flanges or pores must also be taken in respect to the overlapping folds or joints. It is most essential in the case of such joints to remove the last traces of sulphuric acid after anodizing in order to prevent any deterioration of the film and any corrosion patches in the neighbourhood of the re-entrant areas. The same remarks apply quite generally to all objects in which there are overlaps, folds or re-entrant parts where narrow grooves may be present.

Before treating welded parts, care must be taken to ensure that no traces are left of the welding flux, since otherwise, as has been mentioned earlier, there arises on direct current treatment the risk of corrosion. If the weld is clean, direct current anodizing may also be carried out in oxalic acid without hesitation, but it must be remembered that even a carefully made weld, which has been treated in exactly the same way as the neighbouring metal, will frequently

differ in appearance from the surrounding material after anodizing. At the high temperature of welding, variations in structure occur, in the case of many alloys, in the neighbourhood of the weld, and after anodizing these areas present an appearance which differs from that of the areas further removed, which have not been exposed to an equally high temperature. Welded components of this type should not be used for decorative purposes; in such cases other jointing processes—such as, for example, screwing or riveting—must be applied.

It is not possible to undertake directly the anodic treatment of objects which have components of heavy metals, as we have already mentioned. Any heavy metal parts which can be removed before anodizing should be taken off; if such parts are rigidly joined to the light metal they must be covered with an electrically insulating lacquer or cement, otherwise the heavy metal will be dissolved by the sulphuric acid electrolyte. In the case of oxalic acid, small parts of brass, copper or zinc also become covered with a film during the anodic oxidation process, and this film prevents to some extent the further solution of these metals, so that it is also possible to form an anodic film on the light metal joined to these parts, although the film will be thinner than if such metals were absent.[1] This does not apply to iron. Iron goes into solution in the baths used commercially for anodizing and uses up the whole of the current once the first suspicion of a film forms on the aluminium or aluminium alloy, and growth in thickness of the film on the light metal is thereby completely arrested.

[1] According to researches by Messrs. Siemens & Halske A.-G.

CHAPTER XII

COMMERCIAL PROCESSES OF ANODIZING ALUMINIUM AND ALUMINIUM ALLOYS

THE large number of known anodic processes for the production of protective films on aluminium and its alloys led, naturally, to intensive research, which was undertaken with the object of selecting the processes which would be most valuable from the point of view of commercial practice from amongst the large number of possibilities which offered. Apart from the necessity of selecting economic and technically practicable processes, the primary considerations were the corrosion-resistance and mechanical wear-resistance of the films produced. After these the other valuable properties of anodic films were given attention : breakdown voltage, optical reflectivity, heat radiating power, the colour proper of the film and its porosity.

Only a small number of processes emerged from the numerous rival methods which had been proposed : the sulphuric acid process, the oxalic acid process and, in England, the chromic acid process which Bengough and Stuart developed. In Germany only the first two processes have been used commercially, since the chromic acid process has certain disadvantages.

The sulphuric acid and oxalic acid processes possess the great advantage of offering versatility : by a slight change in the operating conditions—for example, by changing the voltage, nature of the current, or the concentration or temperature of the electrolyte—it is possible to induce considerable variations in the nature of the films. There is a further possibility of influencing the effectiveness of the baths by the addition of certain substances to the electrolyte.

Leading German firms have collaborated in the development of anodic oxidation, and have pooled their resources and the results of the researches which they have sponsored. In consequence of this, the " Eloxal "[1] process has undergone rapid development to the important position which it occupies to-day. Moreover, the limiting of the possible processes to a small number which have proved their worth in practical operation has meant that the widest circles have benefited from anodic oxidation, which initially appeared to hold out so many difficulties.

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[1] The word *Eloxal* is derived from the initial letters of the German term " *el*ektrolytisch *ox*ydiertes *Al*uminium," and is used by the firms mentioned for the processes which they operate.

The firms principally concerned with the development of anodic oxidation in Germany (Vereinigte Aluminiumwerke A.-G., Lautawerk, Siemens &·Halske A.-G., Berlin-Siemensstadt, Langbein-Pfanhauser-Werke, Leipzig, and Schering A.-G., Berlin) agreed to pool their resources in order to be in a position to develop commercially the anodic processes which had already been brought to a state of technical maturity, and to continue the development of the processes by mutual exchange of information and co-operative research work. By corresponding arrangements with foreign concerns it was possible also to benefit from the results of research and from the processes and improvements in the field of anodic oxidation carried out abroad. The anodic processes are known in Germany by the generic term " Eloxal " processes, which is used indiscriminately for all of them.

" Eloxal " Processes

The following table summarizes some data in connection with the " Eloxal " processes :

TABLE XXXIV

Process.	Electrolyte.	Type of Current.	Approximate Bath Voltage.	Current Density, amp./dm.^{2}	Bath Temperature, °C.	Time, mins.	Approximate Energy Consumption, kW.-hrs./m.^{2}
GS	sulphuric acid	D.C.	· 15	1·8	20 to 22	30 to 40	0·9 to 1·8
GX	oxalic acid	D.C.	60	1·4	18 to 20	40 to 60	5·6 to 8·4
GXh	oxalic acid	D.C.	30 to 35	1·8	35	20 to 30	1·8 to 3
WX	oxalic acid	A.C.	40	2 to 3	35	40	6 to 8
WGX	oxalic acid	A.C. and D.C.	15 to 30 / 40 to 60	approx. 2 to 4 / approx. 1·5 to 2	20 to 30 / 20	15 to 30 / 15 to 30	2·25 to 7·5

The operating conditions given in the above table are not to be regarded as rigid ; in particular, in the case of the voltages and current densities the figures indicate only the order of magnitude, since, as has been pointed out earlier, the actual voltages and current densities vary with the material (*cf.* Table XXII, p. 136). The temperatures indicated, on the other hand, must in general be rigidly adhered to ; departure from the prescribed temperatures is only permissible if it is desired to obtain special effects. The same applies to the period of oxidation. The bath composition indicated should also be regarded as unalterable, since it represents in each case the

composition which has been proved by experience to be the optimum for commercial practice. It is, of course, essential that the prescribed concentration of the free acid shall be maintained by proper supervision of the bath and by replenishment, where necessary, of the used electrolyte.

If after a bath has been in use for some time an analysis of the effective composition is not available, the voltage which must be applied in order to maintain a given current density for a given material may be determined practically in the following simple manner : a test-piece of known surface (*e.g.* 10 dm.², *i.e.* a test-piece 25 × 20 cm.) is made the anode in the electrolyte, and the voltage is gradually raised until the desired current density is attained. The voltage registered after about 10 minutes' passage of the current is the required working voltage for the material in question and the existing bath composition.

Bengough and Stuart Process

Our description of the anodic processes would not be complete without reference to the Bengough and Stuart process. This was the first commercial process. It was developed in this country just after the Great War, and patents were applied for in 1923 and were subsequently taken out in nearly every country in the world. The electrolyte in this process is a 3 per cent. chromic acid solution whose temperature is maintained at exactly 40° C. The voltage is gradually raised during the period of treatment, which is one hour, the stepping-up of the voltage being carried out at regular time intervals until it attains 50 v. The necessity for " batch " processing which this voltage control introduces is a disadvantage which has to some extent militated against the use of the process since the introduction of the Eloxal processes ; but on the other hand the excellent corrosion-resistance of the anodic film produced, both on aluminium and on duralumin (for the treatment of which a slightly higher current density is generally requisite), has given the process a wide use for the treatment of aircraft parts. A British Standard Specification has recently been issued for the routine carrying out of the process. The film is not very hard and is liable to suffer mechanical injury, but since it is usually sealed with lanoline (see Chapter XIII, Section D) the risk of corrosion attack at any areas which may have suffered abrasion is diminished. The film is dark grey in colour and is therefore not much used for decorative purposes, but the process remains of great importance both in this country and in America for the corrosion-protective treatment of light metal parts exposed to atmospheric and marine influences.

CHAPTER XIII

MOST SUITABLE METHODS FOR CARRYING OUT THE "ELOXAL" ANODIC PROCESSES

THE first point to decide is which process to use in order to obtain anodic films with properties suitable for the use for which they are intended. It may also be necessary to allow for some modifications in the operating conditions set out in Table XXXIV, to suit the material which is to be treated. Finally, it must be remembered that the nature of the pretreatment of the metallic surface of the object and the after-treatment of the anodic film when produced are of almost equal importance in producing the desired results.

Under pretreatment a distinction is drawn between heat-treatment, mechanical pretreatment and chemical pretreatment of the surface. Heat-treatment, which is directed towards the production of a structure in the necessary state of homogeneity and of sufficiently fine grain for oxidation, is in general not the concern of the anodizing works, but of the firm supplying the metal. We shall, accordingly, not deal with heat-treatment here.

After-treatment may include a whole series of separate operations, from rinsing after oxidation to the important procedure of sealing the pores, which has almost always to be carried out. It also includes dyeing and the related process of photo-sensitizing.[1]

The following remarks may be made about the flow sheet on page 192 :

A.—MECHANICAL PRETREATMENT

The grinding, polishing and matt-surfacing[2] of aluminium and its alloys have been discussed by experts in recent literature and will, therefore, not be entered into here.[3]

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[1] By the "Seo" process developed by Messrs. Siemens & Halske A.-G.

[2] For chemical methods of matt-surfacing *cf.* pp. 218-219.

[3] *Cf.* E. Herrmann and E. Zurbrügg, *Die Bearbeitung des Aluminiums*, Leipzig, 1935 ; A. von Zeerleder, *Z. Aluminium*, **17**, 245, 1935 ; A. von Zeerleder and E. Zurbrügg, *Z. Aluminium*, **19**, 366, 1937.

The individual operations are summarized for the sake of clarity in the following flow sheet :
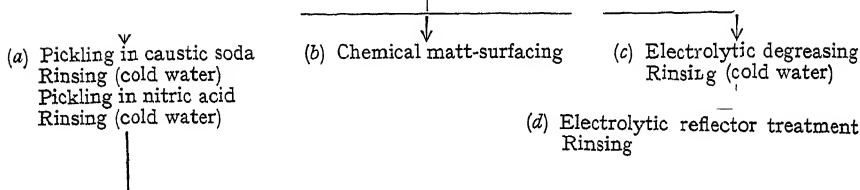
FLOW SHEET OF OPERATIONS.

A. Mechanical Pretreatment.

Grinding

Polishing   Matt-surfacing

Sand-blasting   Scratch-brushing (satin-finishing)
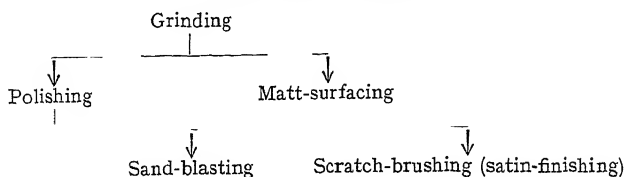
Attaching objects to the contact clamps

B. Chemical or Electrolytic Pretreatment.

Degreasing with organic solvents

(a) Pickling in caustic soda   (b) Chemical matt-surfacing   (c) Electrolytic degreasing
Rinsing (cold water)   Rinsing (cold water)
Pickling in nitric acid
Rinsing (cold water)

                                              (d) Electrolytic reflector treatment
                                                Rinsing

C. Anodizing.

Rinsing (cold water)

D. After-treatment.

Neutralization (ammonia)   Sealing[1] of pores by
Rinsing (cold water)
Dyeing (or photo-sensitizing)
Rinsing (cold water)   (a) Treatment, after   (b) Treatment with
Sealing[1] of pores by   thorough drying,   inorganic mater-
                                                with water-repel-   ials; hot rinsing;
                    or   ling organic media   drying
                                                (fats, oils, etc.)
(a) Treatment, after   (b) Treatment with
    thorough drying,   inorganic mater-
    with water-repel-   ials; hot rinsing;
    ling organic media   drying
    (fats, oils, etc.)

[1] " Sealing " is the term ordinarily applied to direct treatment with media ; the term " filling " is applied if the sealing of the pores is accomplished by indirect deposition by chemical or electrochemical means.

Attachment of the Contact Clamps

Directly after the mechanical pretreatment the objects to be anodized are, as a rule, attached to the contact clamps, from which they are released only after the anodizing and after-treatments have been completed.   In this way fingering of the degreased and anodized surface, which is highly absorptive, is most easily avoided during the numerous manipulations.   The material of the contact clamps must only be pure aluminium or a suitable alloy, such as duralumin, KS-sea-water alloy, Peraluman, Mangal, duralumin K, Legal, Pantal, etc.   It is essential that the clamp shall fit rigidly and shall not be able to work loose during the different manipulations or as a result of the movement of the bath liquid.   The contact must, accordingly, be made by means of a spring pressure of the clamp on the object.   The wire or strip metal used for the clamps must therefore be chosen of a strength such that it can exert the necessary pressure.   If there is any play between the contact clamp and the object the metallic contact between them suffers and hence so does the formation of the film, since there will be oxidation of the areas which have to supply the metallic contact. Moreover, if there is any movement at the point of contact, strong heating may occur in certain cases and give rise to burning at the clamped areas, or to pitting.   The area of metallic contact need in no case be large.   In the majority of cases quite small point surfaces are adequate to maintain the necessary current.   After each use the contact areas of the clamps must be etched clean by immersion in caustic soda ;   the immersion is made as short as possible in order to prevent premature wear of the clamps.   In the case of large and heavy objects it is frequently necessary to use bolts, screws or rivets for attaching the objects ;   all of these must be of pure aluminium or one of the above-named alloys.

If in mass production plants a large number of clamps are continually in use, it pays to insulate the parts which dip into the electrolyte in order to save current.   This is most suitably done by oxidizing the whole immersion surface of the clamps and coating with an insulating acid- and alkali-resisting protective lacquer right up to the contact areas ;   the latter are then treated in caustic soda.   The temperature of the caustic soda used for cleaning the contact areas should not rise above 75° C., in order that the etch may not react on the lacquer.

B.—Chemical or Electrolytic Pretreatment

Objects intended for anodizing must be thoroughly degreased and cleaned, even if they appear clean, in order to avoid any risk of contaminating the anodizing bath.

Degreasing with Organic Solvents

If the objects to be treated are very dirty they are first treated with a grease solvent, such as benzine, trichlorethylene, carbon tetrachloride, etc.—if necessary being scrubbed with a brush. In some cases it is desirable to have two vessels with the solvent for pre-cleaning and after-cleaning. Addition of organic bases to the chlorinated hydrocarbons, which readily decompose in moist air to give hydrochloric acid, is recommended.[1] For the same reason the storage vessels for these liquids must be kept closed.

Pickling in Caustic Soda and Nitric Acid[2]

After wiping and drying the objects, they are treated in a 10 to 20 per cent. hot solution (65° to 75° C.) of caustic soda, which serves the double purpose of saponifying any film of oil or grease which may still be present, and removing the natural oxide skin or that formed by the heat-treatment of the alloys. The vigorous hydrogen evolution which occurs helps the cleaning operation and also mechanically removes any unsaponifiable oils. The precautions necessary to protect the eyes and hands from the strongly corrosive alkali should not be disregarded. The plant should be provided with a good ventilating draught in order to remove the alkaline spray which the gas evolution gives rise to, and which is irritating to the lungs. In the majority of cases a short treatment of half a minute to one minute suffices, and the objects are then rinsed in cold running water and pickled in dilute 10 to 30 per cent. nitric acid. This treatment serves to neutralize any traces of alkali which may remain on the object, and also if the alloys under treatment contain copper it removes the grey to black film of copper oxide formed on the object during treatment in the alkaline bath. The dark-coloured deposit which arises in the case of alloys containing silicon or manganese is not dissolved by the nitric acid, but has to be removed by playing a water-jet over the surface, accompanied if necessary by scrubbing with a soft brush, or by dipping the object for a short space of time in dilute hydrofluoric acid. After the treatment in acid the object must, however, be thoroughly washed in cold running water before it is placed in the anodizing bath.[3]

Removal of the Oxide Film from Objects with Flaws

If the object is one which has already been anodized and exhibits flaws, requiring a second anodizing treatment and preliminary removal of the original film, the same treatment with caustic soda is undertaken to remove the oxide film. If the object has already

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[1] *Cf.* p. 54.   [2] *Cf.* " Matt-surfacing," pp. 218-219.
[3] *Cf.* pp. 218-219 for chemical matt-surfacing.

been greased, it is first freed from grease in the ordinary way in an organic solvent.   If the pores of the anodic film have already been sealed by one of the processes which will be described shortly,[1] difficulties are frequently presented by the removal of the film in caustic soda : and it may then be desirable to give the object a short treatment as cathode in the anodizing bath, using a high current density, and to follow this once again by pickling in caustic soda. It may even be necessary to repeat this treatment.

Electrolytic Pretreatment

The processes for electrolytic pretreatment may be divided into two groups, according as to whether the treatment is cathodic or anodic.   This division is not purely artificial, since it really takes into account the different modes of action of these processes : and, moreover, the processes fall into a natural classification as a result of the different properties and fields of application of the subsequently produced protective films.

1. Electrolytic Degreasing

The processes for electrolytic degreasing belong to the first group.   They are used in order thoroughly to clean polished objects destined for decorative purposes and prepare them for subsequent anodizing, while preserving as far as possible their polish.

The electrolytes used are solutions of different weakly alkaline salts, at room temperature.   The objects are cathodically polarized in the bath for about half a minute, using voltages of 16 to 12 and current densities of 4 to 8 amp./dm.[2]   The containers are provided with an exhaust arrangement to remove the spray caused by the evolution of gas.   They are divided into two compartments by means of a partition, and are equipped with a pump which conducts the liquid flowing from the first compartment over the partition wall into the second compartment, in which is situated a device to remove the greasy substances and dirt coming from the first compartment, and then back again to the first compartment.   After the objects have been removed from the degreasing bath they are well rinsed in running water and, according to the use for which they are intended, they are anodized in the ordinary way.

These degreasing processes, which are familiar also in the field of electroplating, differ in their action fundamentally from the anodic processes described in the following paragraphs.   Their sole action is to induce more rapid and more complete degreasing than is possible with ordinary chemical treatment in alkaline baths, which object is achieved by the help of the vigorous hydrogen

[1] *Cf.* footnote on p. 192.

evolution at the cathode. Moreover, the accelerated treatment which this method renders possible means that the etching action of the alkali may be limited. The application of the electric current allows a uniform distribution of the attack by the alkaline electrolyte over the whole surface, so that the polish on the object is retained better than is possible when the latter is degreased without the application of current.

2. Electrolytic Reflector Processes [1]

The second group of the pretreatments under discussion includes the electrolytic reflector processes, which have recently acquired great technical importance for the production of aluminium reflectors of high reflectivity and extraordinary durability. The problem which was presented of retaining the reflectivity of highly polished aluminium surfaces, and if possible improving it, during pretreatment has been solved only by long and painstaking researches. The development of the processes is still going forward. The idea originated in the U.S.A., and was rapidly followed by research in England and in Germany, where the " Eloxal " combine took it up.

N. D. Pullen has rightly pointed out the fundamental difference in the requirements for a reflector and a mirror. In the case of a mirror, the maximum of reflectivity is required in conjunction with the minimum of diffusion. With a reflector, although the important point is still the achievement of maximum reflectivity, the reflection unaccompanied by diffusion of a mirror may in some circumstances be undesirable, as when the reflector is required to give maximum scattering of light. The degree of scattering depends on the uniformity and flatness of the reflecting surface. It is, however, possible to produce an absolutely plane surface such as is required for a mirror, only on materials which can be ground plane and polished without " flow." This condition, in conjunction with the requirement of high reflectivity and of resistance to tarnish, is fulfilled by only a few materials. The production of optically perfect aluminium surfaces, combined with non-scattering reflection can, accordingly, be achieved in general only by special methods ; for aluminium belongs to the metals whose surface can only with difficulty be worked by ordinary polishing to give a completely plane mirror surface. Attempts have accordingly been made to produce mirror surfaces by special rolling treatment. On the other hand it is sufficient to produce reflectors, where more or less scattering or diffusion does not matter, with a maximum of reflectivity, and to take measures to prevent tarnishing of the surface produced. The problem consists in (1) increasing the reflectivity of aluminium as compared with the normal value ; and (2) protecting the reflecting surface from tarnishing. Accordingly,

[1] Cf. the section on " Reflectivity," p. 148.

we are concerned with a two-stage process, the first stage of which consists in a brightening treatment designed to produce a highly reflecting surface, whilst the second relates to the production of a protective film by means of anodic oxidation.

In the brightening treatment the object is made the anode in an electrolyte, of special composition, which subjects the surface to only a slight etching action, and this, as will later be shown, increases the brightness, whilst at the same time an extremely thin, colourless and transparent oxide film is formed, the existence of which is evidenced only after the surface has been dried by the brilliant interference colours which it exhibits.   The sole function of the anodic treatment which follows the brightening treatment, and which is carried out either in the ordinary way or with slight modifications for the objective in question, is to reinforce the oxide film, and hence to improve the resistance of the reflector to handling or abrasion and to corrosion.   The reduction of the reflectivity necessarily associated with the formation of the protective film can be made extremely small if the anodizing conditions are properly chosen.   In fact, in some circumstances, the reflectivity may even be slightly improved.

H. Schmitt has shown that the treatment in the electrolytic brightening bath in reality produces a smoothing of the surface and an increased lustre, irrespective of how the object to be treated has had its surface produced, that is to say, whether the object has been cast or rolled, extruded or forged, or whether the surface has been emeried, sand-blasted or pickled.   Schmitt demonstrated by microscopic investigation the smoothing effect which the brightening treatment has both on sheets whose surfaces had been cleaned with emery and also on castings of pure aluminium, and showed convincingly that the edges of the " furrows " produced by the emery grains were flattened to a remarkable extent, and that the surface was rendered very nearly plane, any roughening due to the action of the emery having vanished.   This effect of the brightening treatment is fundamentally different from that of etching with the ordinary etches.   After etching an emeried aluminium sheet in sodium carbonate solution or in caustic soda, the surface—in contrast to that produced on electrolytically brightened sheet metal—exhibits bowl-shaped cavities, the deep furrows produced by the emery grains being clearly recognizable under the microscope.

Schmitt explains the smoothing effect of the electrolytic brightening treatment by supposing that a cohesive oxide film forms predominantly on the even areas of the surface, whilst any peaks and sharp edges in the surface are either not covered by the oxide film, or covered only by a non-cohesive film.   These irregularities are more or less removed by the action of the etching component of the electrolyte.   After prolonged etching, which owing to the

electrolyte and the current density chosen proceeds very uniformly, a cohesive oxide film is formed on these areas too.

Taking these factors into consideration, and in view of a process worked out by Figour and Jacquet, who obtained similar brightening effects on copper, lead and other metals by anodic treatment in non-aqueous solutions of phosphoric acid or perchloric acid, Schmitt saw the possibility of developing the brightening process for aluminium beyond its limited use in the production of durable reflectors, to take the place in many cases of mechanical polishing processes.

We shall refer briefly to two of the known reflector processes, the American " Alzac " process[1] and the English " Brytal " process.[2]

In the " Alzac " process, acid electrolytes, such as perchloric acid or chromic acid, with an addition of hydrofluoric acid or other fluorine compounds, e.g. fluorides, hydrofluosilicic acid compounds or fluoboric acid compounds, are used for the brightening treatment, which may be carried out with either D.C. or A.C., better results being obtained, however, with the former. The Aluminum Company of America give the reflectivity after the brightening treatment as 87 per cent. in the case of D.C., and 84·4 or 83·4 per cent. in the case of A.C.   The subsequent anodic treatment is carried out in the " Alzac " process in dilute sulphuric acid.   Edwards states that with the finished product, the brightening treatment having been carried out with D.C., a reflectivity of 80 to 85 per cent. is attainable in commercial practice.

In the " Brytal " process the brightening treatment is carried out in an alkaline sodium carbonate-sodium phosphate solution, whose pH must be at least 10. The objects to be treated are first immersed in this alkaline bath without application of current, in order to pickle them, and afterwards, without being removed from the bath, they are anodically brightened. After removal from the brightening bath they are well rinsed and then given anodic treatment in a sodium bisulphate solution, which provides them with a transparent protective film. This anodizing may be carried out with either D.C. or A.C., and the film formed does not reduce the original reflectivity obtained in the brightening treatment ; Pullen claims that in certain cases the reflectivity may even undergo a slight increase.

The best results from the reflector processes are obtained on aluminium of purity 99·7 per cent. and over. In the case of metal of lower purity the reflectivity obtained is not high enough to meet the requirements of a reflector. Pullen treated a series of aluminium test-pieces whose purity ranged from 99·2 to 99·992 per cent. in exactly the same way by the " Brytal " process, and he showed

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[1] Developed by the Aluminum Company of America.
[2] Developed by the British Aluminium Company, Ltd.

that the reflectivity increased linearly from 99·2 to 99·8 per cent. as the purity of the metal increased. With metal of still higher purity the reflectivity increases less rapidly, as is seen in Fig. 106. Aluminium alloys plated with high-purity aluminium have been used in America for the production of reflectors. In an attempt still further to improve the reflectivity, experiments have been carried out with aluminium alloys. Good results have been obtained in America using an alloy produced from refined aluminium and containing 0·5 per cent. of magnesium and 0·5 per cent. of zinc. Reflectors have also been satisfactorily produced from other aluminium alloys with small alloying additions, *e.g.* the groups Al-Mn, Al-Mg, Al-Mg-Mn and Al-Mg-Si.

After the brightening treatment and the production of the protective film, the objects are rinsed in the ordinary way, and finally the pores are closed by one of the sealing processes described elsewhere.[1] For the use for which the treated metal is intended in this case, treatment with hot water or with solutions of hydrolysable heavy metal salts has proved the most satisfactory, since the reflectivity does not suffer by this treatment. By lightly swabbing the surface with muslin after the pores have been sealed the reflectivity can frequently be still further increased.

FIG. 106.

Reflectivity after " Brytal " Treatment of Aluminium in relation to its Purity.

Aluminium reflectors possess the following advantages compared with those of other metals : light weight, good corrosion-resistance, and resistance to handling and mechanical wear. The latter properties give the reflectors effective protection against tarnishing by chemical attack, atmospheric dust or sand, and against finger-marking, so that it is not necessary to clean or polish the reflecting surface with abrasive cleaners. In most cases light dusting is adequate, but if the reflectors have become dirty due to soot, etc., soaping with a soft, clean sponge and subsequent rinsing with clean water will restore the original quality of the surface. A reduction of reflectivity hardly occurs even at elevated temperatures approaching the melting-point of aluminium. Pullen has stated that a reflector behind a one-kilowatt heating element only exhibited a reduction of reflectivity of 5 per cent. after 1500 hours' use.
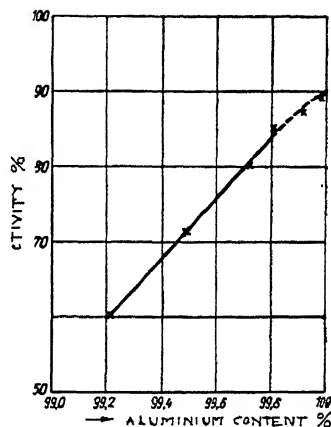
[1] See pp. 204-206.

The reflector processes have already been extensively used in America and England for the production of headlights and searchlights of all types, and for electric and gas heating appliances.

C.—ANODIZING[1]

D.C. Sulphuric Acid (GS) Process

The number of processes using sulphuric acid which have been proposed is very large, which is due to the attempt to suit the properties of the film to the various commercial requirements. Widely different concentrations, ranging from 5 per cent. and less up to concentrated and even fuming sulphuric acid, have been used. In view of the fact that on the one hand a very concentrated sulphuric acid rapidly takes up moisture from the air, until an equilibrium state is reached between absorption of water from the air and, according to the relative humidity, the removal of water from the solution ; and that, on the other hand, a very dilute sulphuric acid gives up the water until this equilibrium state has been reached by evaporation ; it seems best to use a moderate sulphuric acid concentration, which will not undergo any appreciable variation in concentration due to either the absorption or the evaporation of water.

The moderate concentrations of sulphuric acid have, moreover, proved to give, at room temperature, films of high corrosion-resistance and of sufficient hardness to meet the requirements of the majority of applications.   The temperature of 20° to 21° C. at which these concentrations should be maintained can easily be arrived at, since the usual temperature of tap water is about 10° to 13° C. ; and by increasing or reducing the quantity of cooling water, the bath temperature can be modified if it is desired to produce films of special hardness, or films of a porous nature.

Small changes in the bath voltage and current density also offer the possibility of controlling the growth in thickness of the films within wide limits.

The GS process is very versatile in so far as it makes possible the production of films of adequate hardness and of high corrosion-resistance on all the commercially important aluminium alloys. In the case of pure aluminium and on the alloys which have no heavy metal constituents the films are harder than they are on the alloys containing heavy metals such as duralumin, the American and German casting alloys and the aluminium-magnesium-zinc alloys.   Unless influenced by alloying constituents, such as silicon and manganese, or by matt-etching, the films are colourless and transparent.   By virtue of their porosity the GS films take dyes excellently, and this capacity can be increased by raising the bath

[1] This section deals with the German " Eloxal " processes.

temperature to 25° C. In consequence of the transparency and colourlessness of the films, which do not change appreciably the lustre of the underlying metal, the colours produced are clear and bright.

These properties ensure a wide field of application for the GS films. Their use in vehicle construction, in marine architecture and in aircraft, as well as for both interior and exterior architectural applications, has made rapid strides.

Anodic oxidation by the GS process has also found wide use in the light metal piston industry. O. Summa has recommended the anodizing of the machined pistons in 10 to 20 per cent. sulphuric acid to which is added oxalic acid. In the case of the hyper-silicon piston alloys, an increase in the diameter of the piston of the order of 0·01 mm. must be reckoned on, and proper allowance should be made for this when the pistons are produced. The oxide film has a powerful capacity for taking up oil, with very favourable results for the running properties. The film is not hard enough to produce wear of the cylinder wall and, on the other hand, it is hard enough to prevent any particles from the oil sump adhering to it, as they do in the case of untreated piston surfaces, where they behave in the same way as particles of emery and bring about premature wear, even of hard cylinder walls. Researches have shown that, as a result of the good heat radiation of the film, the temperature of anodized pistons remains low (e.g. 60° C.). The frictional values which have been obtained on pistons after allowing them to soak up oil are very favourable. The advantages mentioned are most effective with cold starting, and in this case even use of excess of petrol will never completely remove the oil from the film.

D.C. Oxalic Acid (GX and GXh) Processes

The only essential difference between the GX and the GXh processes is in the temperature of the oxalic acid bath, which in the case of the latter process is maintained at 35° C. In this process the voltage is raised to 30 to 35 in order to maintain the requisite current density. With both processes the period of treatment depends on the requirements.

On pure aluminium and on the alloys containing magnesium, the GX process gives extremely hard, yellow films. It is, therefore, used for the treatment of surfaces which are exposed to sliding friction, such as taps, cocks, screw-threads, etc. The corrosion-protection afforded by the sealed films suffices for the most rigorous conditions. Because of the yellow colour which these films possess, they are only suitable for dyeing to dark colours, particularly black. Light colours are better produced on the GS and GXh films, on which they are clearer and more brilliant. If the bath is properly cooled— particularly if care is exercised to cool the interior of the object

treated—and if the anodizing is carried on long enough, the GX films may attain several tenths of a millimetre in thickness.

The GXh process yields softer films than the GX process ; they are light-coloured—in fact almost colourless on pure aluminium and on the alloys free from heavy metals. The slight yellowish tinge which they possess gives the metal a warm colour comparable with that of German silver. The absorbability which these films exhibit for liquids, dyes and light-sensitive substances is very good, so that they are suitable for dyeing and for photographic purposes (" Seo " process). The films are not so thick as those produced by the GX process, but their corrosion-resistance after sealing of the pores is very good.

A.C. Oxalic Acid (WX) Process

The WX films are appreciably softer than the foregoing films and may be bent without giving rise to cracks, so that they are suited for the protection and insulation of wire and strip. The films produced on pure aluminium and on a large number of alloys are of the colour of brass to bronze, the depth of colour increasing as the current density is increased. The WX process has been recommended for the treatment of welded parts in order to avoid the attack which frequently occurs if welds are treated by the GX process ; but it may be said that no such attack occurs in the GX process if the weld has been properly produced, and if the flux has been completely removed afterwards.

In general practice, anodizing with A.C. is carried out using two carrier bars connected to the terminals of the A.C. source, both being attached to objects which are to be treated—and care being taken that the surface of the objects at the two carrier bars is the same.[1] The voltage is gradually increased, commencing at about 20 and being raised to 50 or 60. According to the use for which the film is intended, the period of treatment is 30 to 60 minutes. The temperature of the bath is ordinarily maintained at 18° C. More flexible films have been obtained on wire and strip at elevated bath temperatures of 40° to 45° C. ; in this case the voltage is kept at 30 to 40. The period of treatment depends on the purpose of the wires or other objects.

The corrosion-resistance of the WX films is sufficient for many purposes.

Combined A.C.-D.C. (WGX) Process

Where specially high corrosion-resistance and hardness are required, the WX process is combined with the GX process to give the WGX process—the types of current being applied in the order named, that is to say, starting with A.C. treatment.

[1] *Cf.* the remarks on p. 113.

This combination gives the possibility of varying the hardness and corrosion-resistance of the films within wide limits according as to whether one or other process predominates. The basic yellow colour of the A.C. film is not changed by the subsequent D.C. treatment. In this process, also, the temperature of the bath is ordinarily maintained at 18° to 20° C. It is hardly necessary to point out that the plant for this process is more costly than in the case of the D.C. process ; so that it is only used in cases where equal results cannot be obtained with other processes.

Mass-anodizing of Small Parts

Where small articles, such as rivets, screws, etc., which have a round and more or less complicated form, are to be treated, cylindrical perforated drums, in which the parts are placed, are used. Contact with the anode is provided by means of an aluminium rod which passes through the axis of the drum, and which connects to the contact plate. The drum, when filled, has a cover fitted in it, which presses the small articles together, so that no film can form on the point contact areas. This is not a disadvantage, since there must be contact points in any anodic oxidation. The method saves the labour of handling the small objects individually, which becomes more difficult and more time-consuming the smaller the articles are. The method is not suited for anodizing objects which have flat surfaces, for the obvious reason that where such surfaces are in contact, no film would be formed. Before the aluminium contact rod is used again, it and the contact plate must be pickled in caustic soda.

In this connection reference may be made to the recently introduced processes for anodizing Zipp fasteners. Among these processes is one in which the Zipp fasteners, after being stamped out from a metal strip, remain unseparated and are detached from the surrounding metal only after being anodized, or in some cases after being dyed.

Rinsing and Neutralization

After anodizing every object treated must be thoroughly rinsed in running water. If pores or joints are present, it is desirable to make sure of removing any acid residues by immersing for a brief time in a 1 per cent. ammonia or ammonium bicarbonate solution to neutralize them, after which the objects must again be thoroughly washed.

D.—AFTER-TREATING ANODIC FILMS

Any after-treatment of the film should preferably be carried out immediately after the anodizing is completed : this applies more particularly to objects which are to be coloured with organic dyes,

since the freshly formed films take up the dyestuffs better than films which have been dried and allowed to stand in air. If immediate after-treatment is not possible the anodized objects should be kept in a warm room, or preferably in a heated drying chamber, and dried at 50° to 60° C. It is not desirable to leave objects which are intended for subsequent treatment longer than about 15 minutes in running water, since otherwise matt areas may be formed in the film which will give the finished object a patchy appearance.

(a) Sealing of the Pores

Sealing of the pores should be carried out as a routine treatment on all anodic films, for it is often the deciding factor in the production of good corrosion-resistance and is absolutely essential to give the films the necessary resistance to handling. In the case of anodized pistons and in similar cases where it is desired to retain porosity, the sealing treatment must not, however, be carried out, and in these cases it is adequate to treat the objects with vaseline, paraffin oil, etc., which renders them impervious to handling whilst at the same time leaving the pores not completely sealed.

The sealing of the pores is invariably the last process carried out in the anodizing shops, whether it is to be followed by a further after-treatment such as dyeing or photosensitizing or not.

A distinction may be drawn between two fundamental types of pore-sealing :

(1) The films are allowed to soak up water-repelling media such as fats, oils or waxes, i.e. organic materials. Treatment with lacquers (which should be very much diluted in order to penetrate the pores properly) is included in this category.

(2) Treatment with inorganic substances such as water, solutions of dichromate, water-glass or hydrolysing salts such as aluminium, cobalt or nickel salts, at higher temperatures.

Sealing of the Pores with Water-repelling Substances

Before the films are treated with fats, oils or waxes, the film must be thoroughly dried. The drying should preferably be carried out at temperatures of 50° to 60° C. Traces of moisture in the film may give rise to patchiness, due to the formation of emulsions formed by the oils or greases with the water. Whitish, dull patches are formed in this way in the film, and it is only rarely possible to remove the patchiness by cautious heating over a flame. Where the film is spoiled in this way, there is no remedy other than to strip the film off and to reanodize the object, or to reject it.

Corrosion tests have been carried out on films treated with different organic substances, and it has been found that vaseline,

lanoline (which is to some extent soluble in water) and most liquid oils do not give adequate protection if the corrosion requirements are high. In the latter case the best results are given by linseed oil varnish, which, as is known, is converted to the tough, solid linoxyn on exposure to air and to the action of light.

Sealing of the Pores by Treatment with Inorganic Substances

When inorganic substances are used, the sealing of the pores may be carried out in two different ways. In one case inorganic compounds are deposited in the pores; in the other case oxidation of the metal on the pore walls occurs. In both cases the film undergoes a simultaneous change as a result of the action of the hot water, in which the pores are greatly diminished in size and/or sealed.

Sealing with Hot Water

This process simply consists in immersing the anodized object for 10 to 20 minutes in boiling water. After it has been removed from the bath and dried, a moistened finger will no longer mark the film and the tendency to form patches is markedly reduced, as is also the ability of the film to take up dyestuffs; the corrosion-resistance is considerably improved. The water used should preferably be distilled and must be neutral. The hydrogen-ion concentration of the water should be determined from time to time.

It has also been proposed to give treatment for 10 minutes with superheated steam (at about 5 atmospheres excess pressure). For obvious reasons this process has not been introduced in practice.

When the hard GX and GS films are treated in this way with boiling water or steam, fine hair-cracks form, but these appear to be without influence on the corrosion-resistance, since the cracks have undergone the same sealing as the pores.

Sealing with Water-glass

The anodic film is immersed in a dilute water-glass solution, after which it is dipped in dilute acetic acid. This treatment results in the deposition in the pores of silicic acid and the formation of sodium acetate, which is removed by the washing water. The process is principally used where porous castings have to be treated. It is not very suitable for decorative purposes, since it is difficult to arrive at a sufficiently uniform precipitation of silicic acid to prevent the appearance of spots or patches in the film.

Sealing with Dichromate

Considerably better corrosion-protection than that obtained by the foregoing methods is afforded by treatment with a very dilute solution of potassium dichromate. The object is allowed to remain for 10 minutes in the boiling solution and after removal is immediately dried. This treatment colours the film yellow; it is accordingly not in general suitable for dyed objects. Where a good corrosion-protection is desired and where the yellow colour is immaterial it is an excellent process to use because of its simplicity. The dichromate solution must be kept completely free from sulphuric acid.

Sealing with Hydrolysing Salts

A solution of a salt of a weak acid with a weak base is used with the addition of a buffering agent. The objects are treated for 10 to 20 minutes in the solution, which is kept very hot, either at 95° C. or boiling. The products of hydrolysis of the solution deposit in the pores of the film as metallic hydroxides. This treatment is very efficient; and the hydroxides formed do not give rise to any coloration of colourless films, so that the process may be used both for uncoloured and for dyed films. The pH value of the bath is of great importance in this treatment and must, therefore, be checked from time to time; solutions which become acid should be brought back to the prescribed pH value by small additions of ammonia, and the water evaporated from the solution should be frequently replaced. The heavy metal content of the bath in question falls off in use as time goes on, and it is, therefore, necessary to institute an analytical control of the bath from time to time, and to replace any salt which may have been used up.

It frequently happens that the metal hydroxides deposit a fine coating, matt in appearance, on the surface of the film, but this can be removed by gentle polishing of the surface with a soft rag. The corrosion-protection of films sealed by this process is adequate for the most rigorous conditions.

(b) Dyeing

The possibility of dyeing anodic films with organic dyestuffs was discovered by Bengough and Stuart, who took out a patent on the subject in 1923.[1] The best films for dyeing are, however, the colourless films, produced, for example, by the GS or GXh process, since they alone give pure and brilliant colours. The colour intensity depends primarily, as has been shown by comprehensive research, on the thickness of the film. It is obvious that a thick film is capable of taking up more dyestuff than a thinner film with the same number of pores of equal diameter. Where it is desired to produce full, deep colours, it is accordingly best to raise the current density

[1] *Cf.* p. 190.

somewhat in the GS process and to prolong the period of anodizing in order to arrive at the thickest possible films.   In the case of pure aluminium, the maximum dyeing capacity is attained at current densities of about 2 amp./dm.[2] and 40 to 60 minutes anodizing period.   The temperature of the anodizing bath is not of such great importance in connection with colouring.   In the case of the GXh process, it is unnecessary to introduce any modifications in the operating conditions, since these are already such as to produce films with excellent dyeing properties and ability to take up light-sensitive substances.   In general the more or less yellow-coloured films produced by the WX, GX and WGX processes are suitable for dyeing only with yellow shades or dark colours, more particularly black.

After anodizing and rinsing, which if necessary is followed by neutralization in 1 per cent. ammonia solution and a second rinsing, the objects are left with the contact clamps in position and are immersed in the dye baths with these.   Rinsing must in no case be carried out in hot water, which, in consequence of the pore-sealing effect, markedly diminishes the ability of the film to take up dyestuffs.   Since no film is formed at the contact points of the clamps, and accordingly no dyestuffs can be taken up at these areas, care should be taken when attaching the clamps to choose positions which will show as little as possible in the finished object. If pores or grooves are present, due to overlaps or flanges, the difficulties mentioned earlier[1] must be overcome ; and it may be necessary to use the GXh instead of the GS process.   The cut edges of polished sheets or other parts may also give rise to trouble on dyeing ; remains of the polishing paste, grease, etc. may remain on these rough areas, in spite of scrupulous degreasing, and may spread into the film to a considerable distance during oxidation.   Little or no dyestuff is taken up at such areas, so that the finished dyed surface appears patchy.   Any cut edges should, therefore, be most carefully ground, or else cutting should be done with special care after polishing and degreasing, in order to ensure that the surface and the cut edges are not further contaminated.

Colouring processes are divided into two fundamentally different processes :

   (1) Colouring with organic dyestuffs.
   (2) Colouring with body colours or pigments.

Colouring with Organic Dyestuffs

In general the dyestuffs used for the colouring of anodic films are water-soluble, oil-soluble dyestuffs being only rarely used, in special cases.   The prime factors in the choice of a dyestuff are the requirements that it shall be adsorbed in large amount by the oxide

[1] *Cf.* pp. 185-186.

film, that it shall not be capable of being washed out by cold or hot water (that is to say, that it shall be fast to washing) and that it shall be fast to light.   Finally, the dyestuff must be resistant to the usual sealing media.   Of the large number of dyestuffs which have been tried, only a comparatively small number have proved to meet the requirements of being wash-proof and fast to light—in other words resistant to atmospheric action.

The concentration of the dye-bath varies widely and depends principally on the solubility of the dyestuff.   Care must be exercised that the dye-bath never contains any undissolved particles, since any such particles may adhere to the surface of the film, causing a non-uniform, mottled or patchy colour.   The concentration of the dye-baths depends also on the nature of the dyestuff.   The more concentrated the solution of the dye, the greater is the life of the bath.   The most favourable temperatures for dyeing likewise depend on the nature of the particular dyestuff, and vary between 60° and 95° C.   Every freshly produced dye solution possesses a characteristic pH value.   Variations in this value may occur after the bath has been in continued use, and these may reduce the bath efficiency. Care must be exercised in handling the baths to make sure that any contamination is excluded.   Thorough rinsing of the anodic films is of first importance, in order to prevent entry of acids or alkalies into the bath ; if this precaution is neglected, these contaminations become enriched as time goes on and may bring about a large change in the pH value, which will ultimately cause flocculation of the dyestuff, rendering the solution completely unusable.   The hydrogen-ion concentration characteristic of each dyestuff must be carefully maintained in order to produce uniform dyeing.   The results of research have shown also that there is an optimum pH value for each dyestuff, at which the best adsorption of the dyestuff and the best wash- and light-fastness are obtained.[1]

The depth of colour produced when the films are dyed can be controlled without difficulty by varying the concentration of the dye-bath, the thickness of the film and the period of immersion of the object in the dye-bath.   In order to ensure that the dyestuff has completely penetrated the film—by which the fastness of the colour is improved—it is necessary to leave the object in the dye-bath for a considerable time ; in general 10 to 20 minutes is a sufficient period.   In order to produce uniform coloration it is desirable to move the object to and fro in the dye-bath, particularly at the commencement of operations.   It is even better to keep the dye-bath agitated by compressed air.   The scum which forms on the surface of the bath must be carefully removed ; otherwise when the object is taken out of the bath particles of scum adhere to the film and give rise to specks.

[1] According to experiments by Messrs. Siemens & Halske A.-G.

Out of a large number of dyestuffs which have been tried the following fundamental colours have proved to be fast to light and washing and to suffice for the majority of purposes : black, blue, green, yellow, two different reds, yellowish-brown and reddish-brown. Mixed shades can be obtained in two different ways : either the object is treated first in one bath and then in another, after intermediate rinsing, which processing requires considerable practice to effect the colour-matching of different objects ; or, better, with a mixed solution of two dyestuffs—provided, of course, that they do not precipitate one another. If it is required to produce patterns, regular or irregular, with two or more colours, various methods are available. Certain of these depend on printing the anodic film with a printing colour not taken up by it, after which the unprinted part is dyed and the printing colour then removed from the printed area by suitable solvents. It is also possible to print a previously coloured anodic film and decolorize the unprinted area, *e.g.* with nitric acid, re-dyeing this area with another dyestuff after washing with water. Thus, after the printing colour is removed, two-coloured patterns may be obtained. This process offers numerous possibilities for the decoration of inscriptions and patterns and is widely used. Another method of producing a coloured pattern depends on the Batik process, in which part of the anodic film is treated with oil, whilst other parts are left free from oil.[1] The latter part of the surface may be dyed with one or more colours, whilst the oiled areas of the surface do not take up the aqueous dyestuff. This process likewise allows of great variation in manipulation. Methods depending on the use of spraying and dropping apparatus or on the use of stencils also open up wide possibilities for producing regular and irregular coloured patterns.

Where objects composed of several parts have to be dyed, a uniform coloration of all the parts is possible only if all of these are of the same material. If this is not the case the differing thicknesses and differing intrinsic colours of the films may give rise to great deviations in the quality and depth of the colour.

Sealing of the pores of dyed objects is as indispensable as in the case of uncoloured films, and for the same reasons, which have already been given ; it serves, moreover, to improve the resistance of the dye. The precaution must, however, be taken of treating each colour separately, in order not to interfere with fastness to light and resistance to water. It would not be wise, for example, to use linseed oil varnish to seal the film in the case of all colours, since the oxidation products of the oil may cause complete bleaching of a dyestuff. The best results have been obtained by sealing with hot water or hydrolysing salts.[2]

[1] This process has been developed by Messrs. Siemens & Halske A.-G.

[2] *Cf.* pp. 205-206.

For colouring with inorganic pigments, films which have specially good sorbing properties are necessary, and these are obtained by using rather higher current densities and bath temperatures than are normal during anodizing.

The pigments are introduced into the pores by allowing the anodic film to imbibe in turn the solutions of two substances which, by double decomposition, form an insoluble precipitate of the required pigment in the pores. It is necessary to rinse the articles in between the two bath treatments, in order to remove the first solution from the surface of the anodic film, since otherwise a thin layer of the insoluble pigment may form on the film surface and prevent the penetration of the second solution. If necessary the treatment in the two solutions may have to be repeated. As in the case of colouring with organic dyestuffs, a certain time is necessary to allow the solutions to penetrate to the base of the film; and it is, of course, obvious that this type of colouring with inorganic pigments requires longer and is, therefore, more expensive than dyeing with organic dyestuffs. The process requires, moreover, some practice and experience to produce satisfactory results.

Almost the whole range of colours may be produced by this process. The resistance to weathering of the films is, in the majority of cases, excellent, although again in this case if the service conditions are to be rigorous a proper choice should be made. The following colours may be produced : black, blue, red, yellow, brown, white, green. A completely dead white is not readily obtained ; as a rule the white is translucent and, because of the metallic lustre which is visible, resembles mother-of-pearl.

The sealing of the pores is accomplished in the same way as in the case of films coloured with organic dyestuffs. Sealing with linseed oil varnish gives good results, also, with inorganic pigments.

C.—The " Seo " Photo-process

This process consists in depositing light-sensitive substances in the pores of the anodic film. The anodic film treated in this manner replaces the carriers for the photosensitive substances which have previously been used in photography, *i.e.* the usual organic colloids, such as collodion, gelatin, albumen, gum arabic, etc. It is at once obvious that in view of the chemical and mechanical stability of anodic films and the absence of organic materials, photographs on aluminium present a number of definite advantages compared with the photographs produced up to now using the ordinary methods of photography.

The way in which the light-sensitive substances are introduced into the film is exactly similar to the processes of dyeing. In this

case also, a differentiation is made between water-soluble and insoluble light-sensitive substances. If the former are in question, it is sufficient to allow the film to soak up the solution and, after removing the excess liquid from the surface, to dry the treated material in a hot-box in order to obtain a film ready for photographic exposure. In the second case, where dealing with light-sensitive substances insoluble in water, the treatment is carried out in the same way as in the deposition of pigments : the film is treated in turn in two solutions which, by double decomposition, give rise to insoluble light-sensitive substances which become incorporated in the pores of the film. After removing the excess of liquid and drying, the film is ready for exposure behind any negative. The subsequent chemical treatment of the exposed film depends on the nature of the light-sensitive substances which have been used and does not differ fundamentally from that ordinarily used in photographic processing.

The most suitable material for the " Seo " photo-process is hard-rolled, pure aluminium of anodizing quality, which does not give rise to streakiness or graining after anodizing—which is equivalent to saying that the metal possesses a fine-grained homogeneous structure. The purity of the metal must be at least 99·5 per cent. Alloys are in general less suitable, unless in special cases corrosion-resistance to sea-water is particularly desired, when special alloys may be used. Duralumin and alloys containing silicon are unsuitable, the latter because of the grey colour which the film possesses. In general, aluminium itself is to be preferred to the alloys on grounds of cost.

Of the different films, the GXh " Eloxal " film is the best. It has a remarkable ability to absorb light-sensitive materials and gives deep, non-translucent colours. Black tones cannot be obtained on the GS films, so that they are only rarely used ; and with the GX films the yellow intrinsic colour spoils the effect, so that these films are used only in cases where high abrasion-resistance is required and where the yellow coloration is not objected to. By combining different anodizing processes, films suited for the production of the most varied photographic effects can be obtained : transparent films, such as the GXh film, in which the metallic lustre is retained in almost unaffected brilliance ; matt or semi-matt films, in which a slight lustre from the underlying metal still persists.

Impregnation with light-sensitive substances and photochemical treatment will be illustrated by some examples in the following.

For ordinary blueprinting, an anodized aluminium sheet is treated with a solution containing potassium ferricyanide and green ferric ammonium citrate. After the sheet has been taken out of the solution and the excess fluid removed from its surface by wiping with a clean cloth, it is treated in a hot-box. It is now exposed under a negative for 1 to 2 minutes in direct sunlight, and developed and

fixed in the usual way with water. On colourless films the blueprint comes up with great clarity and brilliance. The iron gallate process (used in photo-duplicating) may be carried out in a similar simple manner. The solution used in this case contains ferric tartrate as the light-sensitive substance, in addition to other constituents. In this process, as also in the argentotype process, the treated film is exposed for about 10 minutes in direct sunlight and developed in the ordinary way with gallo-oxalic acid or with potassium oxalate solution, respectively, no special fixing solution being required.

In the case of the silver halide processes two solutions, and in many cases also a third, are necessary. The anodized sheet is first immersed in a solution of ammonium chloride and tartaric acid, excess of liquid being then removed from the surface of the film before it is immersed in a silver nitrate solution. After removal from the silver bath it is washed in running water to remove any excess of silver nitrate and dried in a hot drying room. The photosensitivity of the film can be increased by adding bromides and iodides to the first bath. Exposure is carried out in the usual way. In the case of silver chloride-bromide films it is usual to employ a 2-kilowatt arc lamp, which should be at a distance of 250 to 260 cm. from the film, and the exposure period should be from $\frac{1}{2}$ to 1 minute. The picture is developed in an acid " physical " developer, which brings up all the details and gives extremely fine half-tones. The ordinary solutions used in the photographic industry for fixing, toning or reducing may be employed with the usual technique or, in some cases, with a slightly modified composition. There is one exception, namely, all mercury compounds are excluded.

In order to impart the necessary resistance to handling and to corrosion to photographs on aluminium, sealing of the pores is indispensable. Researches by Messrs. Siemens & Halske A.-G. have shown sealing with hydrolysing heavy metal salts to give the best results for this purpose. If another treatment is desired, the photograph may be coated with a dilute colourless lacquer which is unaffected by sunlight.

Experience up to the present has shown that photographs properly produced by the " Seo " photo-process may be regarded as completely resistant to weathering. They are also resistant to sea-water, if care is taken that the edges are smoothed and are coated with a protective film. The photographs are unaffected by organic solvents, such as alcohol, ether, benzene, amyl acetate, etc.

A valuable property of the photographs produced with silver halides is their remarkable fire-proof quality. A properly produced gold-tone photograph will stand heating over a Bunsen flame up to and above the melting-point of aluminium (659° C.) ; the original black colour of the photograph becomes a reddish hue—a tone reminiscent of purple of Cassius—but for the rest the photograph

is unaffected and remains clearly visible on the oxide film, which sinters only at a much higher temperature (1700° C.).

The change in colour produced by heating is due to a variation in the size of the gold particles. It does not take place instantaneously but the colour transition proceeds gradually as the temperature is progressively raised. At 100° C., already, the colour changes from deep black to brownish-black, and then undergoes further change to light brown and brick-red as the temperature rises. Finally the red takes on a bluish tinge after becoming wine-coloured or crimson. The colours produced on heating may be greatly influenced by varying the time in the gold bath during the original toning process ; or by treating the fixed, untoned silver photograph in solutions of heavy metal salts and subsequently heating them, a great variety of colours may be obtained. Thus uranyl acetate gives full rust-brown tones, whilst lead salt gives a deep black. Blueprints may also be given a variety of colours : by immersing in lead acetate solutions, washing and treating with potassium dichromate solution, a brilliant grass-green may be obtained ; or a violet colour can be produced by treatment with copper sulphate solution followed by washing with water, and this violet can be transformed to dark brown by treatment with sodium sulphide. In general, the majority of toning processes used in the photographic industry can be applied to photographs on aluminium.

In view of the variety of colours which can be produced, the possibility presents itself of preparing multi-coloured pictures by purely photographic processes. Moreover, by combining the " Seo " photo-process and dyeing processes a very wide range of effects may be obtained, the unexposed areas of the picture being coloured by hand or by printing. By printing with a glazing, non-covering colour the black of the " Seo " photograph remains in almost its original depth of tone. In this way, multi-coloured scales can be produced without difficulty.

The remarkable properties of photographs on anodized aluminium have opened up a wide range of applications not open formerly to photography. The more important applications are reviewed in the following summary.

(d) Summary of the Applications of Anodized Light Metals

The low specific gravity of the light metals has given them *a priori* a great advantage as the constructional materials for all types of vehicles and transport units on land, on sea and in the air, so far as their tensile strength permits. In addition, pure aluminium has found wide use for the most varied utility and household objects. The processes for the production of corrosion-resistant and mechanically resistant protective films on aluminium and its alloys

have still further extended the possibilities of using light metals. The other valuable properties of these films, which have been discussed in the foregoing chapters, have contributed steadily, and to a growing extent, to the development of new fields of use for aluminium and its alloys. The possible applications are already so numerous that any attempt to deal with them in detail would be outside the scope of the present monograph. The best way of discussing the applications would seem to be, for the sake of brevity and to provide a conspectus of the situation, to indicate in tabular form the principal industries which make use of anodic oxidation, merely outlining the types of individual applications.

To make the survey clearer, some explanations will be added. The applications are divided into two principal groups (I) and (II) according as to whether the films in question are (I) sealed, *i.e.* with pores closed, or (II) unsealed, *i.e.* with pores open.

This division appears justified since sealed films are no longer suitable for treating with dyestuffs, pigments or light-sensitive substances, and have to a large extent lost their original value as an adhering base for paints and lacquers. Although the pores must be sealed after dyeing or photographic treatment to ensure resistance to corrosion and handling, and in some cases the sealing must be carried further by applying a coat of paint or lacquer, the choice of these processes depends exclusively on the porosity.

The subdivision into groups of applications under the main headings (I) and (II) is readily arrived at.

In Group (I) the subdivision is arranged according to the properties of the film, each property being considered in respect to the applications based on it, irrespective of whether the same applications reappear under another heading. Since corrosion-resistance and hardness or abrasion-resistance taken together determine most of the technical applications of anodized parts they are given the first and largest sub-group A. Similar categories of sub-groups are based on the properties :

B. Electrical insulating and dielectric properties.
C. Light reflectivity.
D. Heat emissivity.

In Group (II) the subdivision is arranged according to the nature of the substances taken up by the pores :

A. Sorption of organic dyestuffs or inorganic pigments for the purpose of colouring the films.
B. Sorption of light-sensitive substances for photographic purposes (" Seo " photo-process).
C. Sorption of lubricants with the object of reducing the friction of sliding contact surfaces.
D. Sorption of constituents of paints and lacquers by way of the pores (rendering the films suitable as a basis of adherence).

This subdivision gives four sub-groups, A to D, for each main group, the further subdivision being as shown in the table and requiring no explanation. The first sub-group A of Group I dealing with transport units is the only one requiring any further differentiation on the basis of the materials used. The subdivisions (*a*), (*b*) and (*c*) are based on the following :

- (*a*) relates to forged metal in the form of round rod, wire, sections, pressings, tubes, etc. ;
- (*b*) forged metal in the form of sheet ;
- (*c*) castings.

In connection with the references in the table to screwed parts, mention should be made of an article by Bauermeister and Kersten. These authors recommend, as a result of their investigations, anodizing not only of the screws but especially also of the nuts or seatings when dealing with screwed joints of aluminium alloys, since the oxide film is resistant to corrosion and is, therefore, the best means of preventing the parts from corroding together. Bollenrath and Gröber express the same opinion ; and they further recommend the anodizing of ships' screws or propellers, since the hard anodic film serves to prevent not only corrosion but also cavitation. The idea should not be dismissed lightly but is of considerable interest for the high-duty casting alloys of the Al-Mg and Al-Mg-Mn classes, which are resistant to sea-water, and the films on which are extremely hard.

Tabular Survey of the Applications of Anodized Light Metals

I. SEALED FILMS
(pores closed)

A. Corrosion-protection, Hardness, Abrasion-resistance.

1. Constructional Parts and Fittings for Transport Units of all Types.

Land Transport.	Marine Transport.	Air Transport.
Railway rolling stock, tramway stock, motor-car, cycle construction.	Marine construction.	Aircraft construction.

- (*a*) Pillars, brackets, hand rails, grilles, door and window frames, doors, picture and mirror frames, hardware, screws, cycle frames, handle-bars and hand levers, spokes ; marine screws, propellers.
- (*b*) Panelling, exterior bodywork, bonnets, fairings, wing surfaces.

(c) Hardware, handles of all types (door and window fittings), luggage rack brackets, coat hooks, light fittings and screw fittings.

2. Military, Fire-fighting and Sports Equipment.
   Drinking flasks, food containers, cooking and eating vessels, buttons, insignia, belt fastenings, uniform ornaments, buckles.

3. Optical Industry.
   Mountings, housings, frames, stands, fittings and parts of photographic apparatus.

4. Office Equipment.
   Parts of typewriters, calculating machines, copying machines, drawing and measuring apparatus, slide-rules.

5. Textile Industry.
   Machine parts, bobbins.

6. Chemical Industry.
   Storage and transport containers, reaction and washing vessels, piping, cooling and heating coils.

7. Saltern Plant.
   Piping, containers, crystallizing vessels, cooling and heating coils.

8. Food Industry.
   Equipment of butcheries, bakeries and breweries, wine presses, jam and fruit processing, transport and storage containers, storage vessels, fermentation tanks, hop holders, cooling plant fittings, boxes for packing preserves.

9. Architecture and Interior Decoration.
   Frontages, shop fittings, bar fittings, wall panellings, door and window frames, hand rails, grilles, pillars, brackets, hardware, picture and mirror frames, furniture, light fittings, taps and various fittings for water supply, door and window furniture, bathroom equipment, coat-hooks.

10. Household and Everyday Objects.
    Culinary vessels and paraphernalia, table ware, refrigerator fittings, plates and stands, trays, shelves, hooks, furniture, and fittings on domestic appliances.

11. Arts and Crafts.
    Bowls, vases, fancy boxes, light fittings, caskets, frames, fittings, stands, ash-trays, chains, necklaces, bracelets, shoe and belt ornaments, Zipp-fasteners, buckles, etc.

12. Objets d'Art.
    Statuary.

B. Electrical Insulating and Dielectric Properties.

Wire and strip for windings and coils in engines, generators, transformers, measuring instruments, safety covers, casings.

C. Light Reflectivity.

Reflectors for all types of headlights and searchlights and for electric and gas heating apparatus.

D. Heat Radiation.

Heat exchangers of all kinds, radiators, pistons for internal combustion engines.

II. UNSEALED FILMS
(pores open)

A. Sorption of Dyes and Pigments.

1. For Decorative Purposes.

Utility objects of all kinds, art objects, coloured sections and sheet for interior decoration and for external architectural fittings, buckles, buttons, jewellery.

2. For Colour-print Processes.

Mono- and poly-chrome printing on inscription plates, number plates, maps and plans, instruction sheets, advertising signs, packing material.

B. Sorption of Light-sensitive Substances (" Seo " photo-process).

1. Inscription plates, scales, graph plates, number plates, maps and plans, instruction sheets, advertising signs, decorative patterns.

2. Half-tone prints of all kinds : pictures, landscapes, views.

C. Sorption of Lubricating Oils.

Bearings, cross-heads, pistons of internal combustion engines.

D. Sorption of Constituents of Paints and Lacquers.

Application as a base of adherence for lacquers, paints and electrically insulating lacquers.

CHAPTER XIV

CHEMICAL SURFACE TREATMENT PROCESSES

CHEMICAL surface treatments of aluminium and its alloys may be divided into two classes, according as to whether the metallic surface is intentionally or unintentionally worn away by the treatment. To the first class belong the processes of etching, pickling and matt-surfacing; under the second are included the processes for the deposition of metallic coatings and the processes for the production of oxide protective films.

Of the processes in the first class, etching lies outside the scope of our considerations, and pickling has already been referred to elsewhere.[1] In the second class, the production of oxide protective films is of direct interest to us and we shall also have occasion to refer to the deposition of metallic coatings. It is not always possible to draw a definite dividing line between these two processes, since they may be used either separately or combined in one process; and also because the reaction products characteristic of the two processes are frequently present in the same film.

We shall proceed to discuss matt-surfacing and, in greater detail, the production of oxide protective films.

(a) Matt-surfacing

The following three processes have proved satisfactory in practice :

(1) Treatment in a hot 10 per cent. sodium carbonate solution. On pure aluminium and aluminium alloys free from heavy metals or silicon, a matt white surface is obtained. Since marks are readily produced by rubbing on the matt surface, it is desirable to protect such matt-surfaced objects by applying a colourless lacquer, unless it is intended to give subsequent oxidation treatment.

(2) Treatment with a hot aqueous solution containing 3 per cent. of nitric acid and about 4 per cent. of sulphuric acid. It is desirable to precede this treatment with pickling in hot 10 to 20 per cent. caustic soda, after which the objects must be thoroughly rinsed in running water. A beautiful matt surface may be obtained in this way, even on the alloys containing copper.

[1] *Cf.* p. 194.

(3) Particularly good results are obtained in a matt-etching solution consisting of one part by volume of saturated sodium fluoride solution and one part by volume of concentrated nitric acid. The solution is used at room temperature, but certain precautions must be observed because of the hydrofluoric acid : good ventilation must be provided, and the vessels used must be lined with vulcanized rubber or paraffin wax, since ceramic material, glass or steel is rapidly attacked.

It goes without saying that directly after matt-etching the objects treated must in all cases be well washed in running water. Matt-etching can with advantage be used as a pretreatment to anodic oxidation to obtain certain effects.

(b) Oxide Protective Films

In the General Part of this monograph we have already referred to the parallel nature of the phenomena which occur during electrolysis at metal anodes and during ordinary contact of a metal with an aqueous liquid where no external current source is concerned. It has been shown that in both cases the processes involved are electrical or electrochemical. This parallel nature of the observed phenomena obtains also in the more narrowly limited field of the processes for the production of oxide protective films. In this case also, electrochemical processes are involved in both anodic and chemical methods. In both cases, in addition to formation of the oxide film, there occurs a wearing-away of the metal surface, which may be due either to the dissolution of part of the film formed or to direct attack of the surface of the metal by the bath liquid. In both cases oxidation processes are involved.

There is, however, an important difference between anodic and chemical treatment, in so far as in properly controlled anodizing no reduction processes occur at the anode ; whilst in the case of chemical oxidation, processes of both oxidation and reduction must necessarily occur at the object under treatment if the purpose of the treatment, to form an oxide film, is to be achieved. The bath must on the one hand contain substances which are capable of attacking the metal with or without visible evolution of hydrogen and on the other hand it must contain substances which convert the aluminium into the difficultly soluble oxide in order to oppose complete solution of the metal. These oxidizing substances are reduced partly by virtue of the fact that they give up their oxygen at the aluminium and partly by the direct action of the hydrogen which is liberated at the metal ; so that their reduction products may, in so far as they are insoluble, contribute to the film formed by being incorporated in the aluminium oxide film as it forms. The so-called " colouring " processes depend on these phenomena.

The following are used as attacking agents in the chemical processes for the production of protective oxide films on aluminium and aluminium alloys : solutions which react alkaline, such as very dilute caustic soda, sodium carbonate, trisodium phosphate or alkali cyanides ; solutions which react acid, such as sulphuric acid, phosphoric acid, acetic acid, hydrofluoric acid and nitric acid (which at the same time has an oxidizing effect) ; also the double fluorides of the alkali metals, and the neutral alkali salts of hydrofluoric acid and of hydrofluosilicic acid.

The following are suitable oxidizing agents : nitric acid (see above), the nitrates of the alkali metals, hydrogen peroxide, chromates, dichromates and potassium permanganate. The chromates and permanganate are reduced by the oxidation process to chromic oxide and managanese dioxide respectively, which become incorporated in the aluminium oxide film to give grey and yellow to brown coloured protective films.

By adding heavy metal compounds to the oxidizing baths, a very wide range of colours and shades may be produced, since the heavy metal compounds are converted on reduction into lower oxides or to metal, which forms part of the film. If only metallic deposition is aimed at, the addition of oxidizing agents can be omitted.

The MBV Process

Of the numerous German and foreign processes for the production by purely chemical means of protective films there is only one which has attained any practical importance in Germany up to the present : this is the modified Bauer-Vogel process, known as the MBV process. The process was developed by G. Eckert at the Erftwerk, Grevenbroich, one of the works connected with the Vereinigte Aluminiumwerke A.-G., as a modification of the original Bauer-Vogel process. Eckert was able to achieve a considerable time-saving in the treatment by omitting the addition of alum which O. Bauer and O. Vogel had used originally, and by using sodium chromate in place of potassium dichromate. By virtue of these changes the treatment time was reduced from 2-4 hours to 3-5 minutes to obtain equally effective results. The bath temperature is maintained at 90° to 100° C. The bath is very economical—10 litres of bath will treat about 32 square metres of aluminium surface—and the cost of the process is accordingly very small. In ordinary procedure, 60 g. of MBV salt is added per litre of water, but this solution may be diluted up to 40 times its own volume and will give excellent protective films if the period of treatment is prolonged accordingly.

The ordinary period of treatment is 5 to 20 minutes ; if this period is lengthened the films formed, say after 1 to 2 hours, are

rougher in appearance, whilst the growth in thickness, which is initially rapid, later slows down considerably.[1] After treatment the objects are rinsed in water and dried. The keeping qualities of the film are improved by treatment in boiling water, and still better results can be obtained by after-treating the film with a 2 to 5 per cent. water-glass solution at a temperature of 90° to 100° C. for 10 to 15 minutes.

The film is light to dark grey in colour and is opaque. On smooth-rolled or polished objects the films have a decided lustre. The after-treatment with water-glass or with boiling water induces a definite lightening of the grey tone.

The process is applicable to pure aluminium and to all alloys of aluminium provided they do not contain copper. If alloys with a high magnesium content are to be treated, an addition of 10 g. of caustic soda should be made per litre of solution containing 60 g. of MBV salt; and in this case the temperature of the bath should be held at 60° to 70° C.

W. Geller points out that in order to obtain a serviceable protective film by the MBV method it is absolutely necessary, as a preliminary, to remove the heavy oxide skin which forms during heat-treatment on alloys of the aluminium-magnesium-silicon type, by chemical or mechanical means. If this precaution is not taken, the corrosion-resistance of heat-treated Pantal sheet may after treatment by the MBV process, as Geller's investigations have shown, be even less than that of the completely untreated Pantal sheet—presumably as a result of a weakening of the original oxide skin during the treatment. This suggests that it is advisable in other cases to remove the natural oxide skin before applying the MBV treatment, in order to prevent failure.

For special cases, such as the protection of rivet heads, which remain unprotected in a joint between two oxidized sections, the application of a paste consisting of 10 parts of sodium chromate, 4 parts of calcined sodium carbonate, 4 parts of caustic soda and 10 to 15 parts of water is recommended. The paste is allowed to remain on the parts to be treated for 10 to 15 minutes, either at room temperature or with the application of gentle heat from a flame, after which it is rinsed off and the object is dried.

W. Helling and H. Neunzig have carried out investigations on the colouring of MBV films. They found that after-treatment of MBV films with MBV solution to which potassium permanganate had been added gave films of light brown, greyish-green, dark brown, or reddish-brown colour. Yellowish-brown, reddish-brown and black colorations were obtained by using a solution in nitric acid of potassium permanganate and copper or cadmium nitrate. Better results from the point of view of fastness to light and exposure

were produced by using cobalt nitrate in place of copper nitrate. In all the above-described treatments, short period heating to 100° to 150° C. improved the chemical resistance of the films. Blue colours could be produced by soaking the MBV film with solutions of potassium ferricyanide and ferric chloride. The colour is originally green, but after exposure to light for some days it changes to dark blue. These colours can be made resistant by impregnating the film, after heating to 100° to 150° C., with an I.G. wax-paraffin mixture, or with a colourless lacquer, such as " Kronogen " lacquer.

Investigations of the change in weight of aluminium test-pieces during MBV treatment and of the relationship between the thickness of the film produced and the period of treatment have been carried out only very recently—incidentally, by different investigators, working independently—published data having previously been, so far as the author is aware, without experimental evidence.

In view of the fact that the MBV film is not very hard, measurement of the film thickness presents difficulties. It is not possible to make the usual microscopic measurement on a section at right angles to the surface, using a micrometer, since the soft MBV film is affected by the grinding operation and a sharp boundary between the metal and the film is not obtainable. The same applies to sections made with a guillotine ; in this case, again, there is no sharp boundary between the film and the metal, so that it is impossible to read the thickness of the film. Measurements of thickness must, therefore, be carried out by other methods : the difference between the total thickness of the treated sheet and of the sheet after the film has been carefully removed is measured with a micrometer gauge.

The Aluminum Company of America has developed a method of removing the film by etching without attacking the underlying metal. The method consists in treating the film in a hot solution of sulphuric acid containing antimony. The point at which the oxide film is completely worn away, leaving the metal surface exposed, is indicated by the appearance of a thin grey- to black-coloured tarnish deposit of antimony. Apart from this indicator action of the antimony it has the additional function of inhibiting the attack by the acid. The treatment is continued for 20 to 30 seconds after the discoloration first appears, the total period of the test occupying 40 to 90 seconds. The quantity of the underlying metal which goes into solution in these circumstances is extremely small and can in practice be neglected.

The figures given in Table XXXV for the thickness of anodic films, which were derived in the one case by optical and in the other case by etching tests, show satisfactory agreement.[1] The comparative measurements were in all cases made on the same

[1] According to researches by Messrs. Siemens & Halske A.-G.

test-piece. The figures show that the etching method in general gives smaller values than the optical method. In the majority of cases the differences are only a few tenths μ, and only in four out of the twelve cases does the difference reach 1μ or over. It is hardly to be expected, of course, that measurement by the etching process of the MBV film thickness, which is in general very small, would give entirely reliable results. In order to correct as far as possible for the inevitable experimental errors an average value from a large number of individual determinations should be taken.

Table XXXVI gives the film thickness as measured by a similar etching process developed by W. Helling. In this case the film is dissolved away by 65 per cent. nitric acid, which, as is known, does not attack aluminium when it is in high or low concentration.[1]

<div align="center">TABLE XXXV</div>

Metal Oxidized.	Film Thickness in μ		Difference.
	By Optical Method.	By Etching.	
Aluminium . . .	6·1	6·3	0·2
	17·7	17·3	0·4
	23·7	21·4	2·3
	37·7	36·0	1·7
	39·8	39·5	0·3
Duralumin . . .	15·3	14·8	0·5
	3·2	3·25	0·05
	8·4	7·4	1·0
	11·6	11·0	0·6
	14·6	15·0	0·4
	17·5	17·3	0·2
	15·5	18·3	2·8

The loss in thickness due to the etching effect was in fact found by Helling to be so small as to be negligible. The tests were carried out on hard-rolled 99·5 per cent. aluminium sheet. Fig. 107 shows the increase in thickness of the film with time during the MBV treatment.

In spite of the growth in thickness, the initial weight of an aluminium test-piece is markedly reduced by the treatment. This decrease in weight, according to the results of different, independent workers, which are in good agreement, is of the order of 8·5 to 10 g./m.[2] surface of aluminium after treatment for 30 minutes.

Helling determined the loss in weight of a number of aluminium alloys on MBV treatment and in some cases found astonishingly high values. Thus, for alloys with a high magnesium content the loss in weight was up to 79·5 g./m.[2] These alloys also give films of remarkable thickness, up to $33\cdot8\mu$. The data derived for the film

<div align="center">[1] Cf. p. 61.</div>

formation on copper-containing alloys, which up till now have been considered unsuitable for treatment by the MBV process, are of particular interest. In the same series of investigations it was found that the thicker and rougher films possess a greater absorbing power for lacquers than the thinner films ; and, correspondingly,
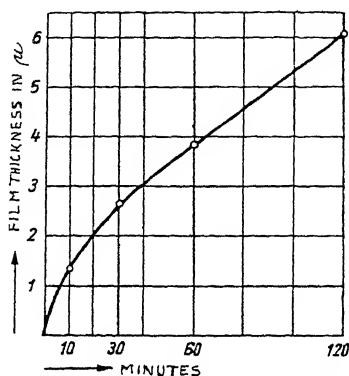
FIG. 107.—Increase in Film Thickness with Time during MBV Treatment.

thick MBV films take up more dyestuff than thin films. The corrosion-resistance to sodium chloride solution of the MBV films is greater the thicker they are. On the other hand, the thick films are less effective as a protection against the action of heavy metal salt solutions than the thin films. Helling concludes from these facts

TABLE XXXVI.—MBV PROCESS

(99·5 per cent. Aluminium Sheet)

Period of Treatment, minutes.	Film Thickness, μ.
10	1·3
30	2·7
60	3·8
120	6·1

that the most favourable treatment time in the MBV bath to produce good corrosion-resistance depends entirely on the nature of the attacking solution and must be determined for each case.

Of the other known chemical processes for the production of protective films we shall refer briefly to those mentioned at the commencement of this chapter, in view of the existence of a large

number of patent specifications, but no discussion will be entered into as to their commercial value. There is no published information within the last few years indicating any practical application in Germany of the films produced by these processes, and it is hardly to be expected that they offer any advantages in comparison with the MBV process or the anodic processes.

Jirotka Processes

B. Jirotka has developed a number of processes for the production of coloured protective films on aluminium, and he has even worked out several processes for treating magnesium and magnesium-base alloys. The baths used consist of acid or alkaline solutions with additions of heavy metal salts whose reduction products are incorporated in the aluminium oxide film, giving rise to a very wide variety of colorations. The heavy metal compounds used to give these colours are the salts of the following metals : zinc, chromium, cobalt, nickel, iron, tin, lead, bismuth, copper, silver, gold and manganese. In a few cases the treatment time is appreciably diminished by using an additional electrode, which is short-circuited with the object being treated. Other processes, in which the added metal salt is reduced to the point at which the metal itself is precipitated, serve to produce novel colour effects or they are in some cases used as a preparatory treatment to subsequent galvanic plating of the aluminium. In alkaline baths, Jirotka finally succeeded in arriving at a reduction which produced coherent, lustrous metal deposits on the aluminium.

Tests in different reputable laboratories have shown the corrosion-protection afforded by the Jirotka oxide films to be good, but the disadvantage of the films lies, as in the case of all the chemically produced films, in their small thickness and poor hardness. Their advantage consists in the economical nature of the process. The films must be regarded as primarily suited for decorative purposes, because of the great variety of colour treatment which the Jirotka processes offer, the colours in some cases being very attractive.

Protal Processes[1]

The Protal processes use alkaline solutions of compounds of those metals which form at least two oxides, the higher of which is soluble in alkali whilst the lower is insoluble. Under the reducing action of the hydrogen liberated at the aluminium the insoluble lower oxide is deposited in the aluminium oxide film. The alkaline solutions contain about 0·5 per cent. of alkali vanadate, molybdate, tungstate, titanate, uranate, niobate or manganate. The free alkali content is 1 per cent. The object is left for about 40 minutes in the bath,

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[1] Invented by Ch. Boulanger ; patents owned by the Société Continentale Parker.

which is kept boiling.   The complex salts which constitute the baths perform the double rôle of acting as oxidizing agents and as colouring compounds, so that there is no necessity to add auxiliary oxidizing agents.   The presence of chromate is undesirable, but an addition of borax had been recommended as giving good results. Neutral fluorine-containing complex salts are also used in the Protal processes.   The effectiveness of the baths can be preserved by adding titanium fluoride to them.

Pacz Processes

A. Pacz employs acids, fluorides or the alkali metal salts of oxalic acid, hydrofluotitanic acid, hydrofluozirconic acid or hydro-fluosilicic acid as the attacking media, and nitrates of the alkali metals as oxidizing agents ; the colouring heavy metal compounds are salts of nickel, cobalt or zirconium, or molybdenum compounds (e.g. ammonium molybdate).   Cathodic treatment of the metal using a zinc anode and additions of ammonium salts to the bath also gives coloured coatings in certain circumstances.   Pacz produced dark-coloured protective films on Silumin by using alkaline solutions of chromates, similar to the MBV bath.   Most of Pacz's processes are directed to the production of coloured metal surfaces, and no information is available regarding the corrosion-resistance of these films.

APPENDIX

BRITISH PATENTS.

IN the following is given a chronological list of the British patents on the anodic oxidation of aluminium :—

223,994	G. D. Bengough and J. M. Stuart.
223,995	G. D. Bengough and J. M. Stuart.
226,536	Zaidan Hojin Rikagaku Kenkyujo.
287,503	Spezialfabrik für Aluminium-Spulen und Leitungen G.m.b.H.
290,901	C. H. R. Gower and Stafford O'Brien and Partners, Ltd.
290,903	C. H. R. Gower.
294,237	Electrolux, Ltd.
329,190	E. W. Küttner.
342,256	C. Boulanger.
352,656	R. E. Müller.
353,558	R. E. Müller.
358,290	British Thomson-Houston Co.
359,494	S. R. Sheppard.
359,495	S. R. Sheppard.
369,059	Vereinigte Aluminium-Werke.
371,213	Siemens-Elektro-Osmose G.m.b.H.
374,806	Vereinigte Aluminium-Werke.
377,385	Vereinigte Aluminium-Werke.
378,521	Aluminum Colors, Inc.
381,402	R. S. Dunham.
382,287	S. R. Sheppard.
383,664	Kolster-Brandes, Ltd., M. S. Hoban and R. W. Strafford.
385,067	Siemens and Halske A.-G.
385,763	Vereinigte Aluminium-Werke.
386,201	Vereinigte Aluminium-Werke.
387,437	A. A. Samuel.
387,806	R. S. Dunham.
388,787	Vereinigte Aluminium-Werke.
390,110	Siemens-Elektro-Osmose G.m.b.H.
391,148	S. R. Sheppard.
391,903	R. S. Dunham.
393,996	R. S. Dunham.
394,637	Siemens and Halske A.-G.
395,390	C. H. R. Gower and E. Windsor-Bowen.
396,204	Aluminum Colors, Inc.
396,745	E. Windsor-Bowen.
397,538	British Aluminium Co., Ltd., A. G. C. Gwyer and A. N. D. Pullen.
398,825	P. R. Coursey, C. H. Marcus and Dubilier Condenser Co.
401,270	Aluminum Colors, Inc.
401,579	Aluminum Colors, Inc.
403,560	Aluminum Colors, Inc.
404,251	Siemens and Halske A.-G.
405,707	L. Cox and Lightning Fasteners, Ltd.
406,988	Aluminum Colors, Inc.
407,208	Aluminum Colors, Inc.
407,457	Aluminum Colors, Inc.
407,670	Mead Research Eng. Co.
407,830	Siemens and Halske A.-G.
409,679	Aluminum Colors, Inc.
412,193	C. H. R. Gower and E. Windsor-Bowen.
412,205	C. H. R. Gower and E. Windsor-Bowen.
413,814	Aluminum Colors, Inc.
418,498	Siemens and Halske A.-G.
421,217	O. Wolf.
423,467	Society of Chemical Industry in Basle.
427,308	P. J. White.
429,344	S. R. Sheppard.
432,984	Siemens and Halske A.-G.
433,367	Peintal S.A.
433,484	Aluminum Co. of America.
436,154	Aluminum Co. of America.
436,270	Peintal S.A.

436,481	Aluminum Co. of America.
436,704	Peintal S.A.
436,854	Peintal S.A.
437,244	Peintal S.A.
438,494	Peintal S.A.
440,287	Aluminum Co. of America.
440,550	Siemens and Halske A.-G.
440,608	Siemens and Halske A.-G.
441,810	Peintal S.A.
442,902	Siemens and Halske A.-G.
447,420	C. H. R. Gower and E. Windsor-Bowen.
447,421	C. H. R. Gower and E. Windsor-Bowen.
449,162	A. N. D. Pullen and British Aluminium Co.
449,175	P. J. White.
449,289	Langbein-Pfanhauser-Werke.
451,742	E. A. Lie.
452,257	Langbein-Pfanhauser-Werke.
455,077	F. Singer.
455,412	M. Schenk.
455,761	Aluminium-Industrie A.-G.
457,037	H. E. Gresham.
459,263	Schering-Kahlbaum A.-G.
459,264	Schering-Kahlbaum A.-G.
460,430	Intertype, Ltd.
460,437	G. M. Argabrite.
462,269	C. Baillod.
463,790	S. R. Sheppard.
464,757	F. L. Impey and Morland and Impey, Ltd.
465,054	British Thomson-Houston Co.
466,941	V. Lichoff.
467,267	G. C. Jones.
468,685	A. N. D. Pullen and British Aluminium Co.
469,571	Schering-Kahlbaum A.-G.
470,734	Vereinigte Aluminium-Werke.
474,323	Schering-Kahlbaum A.-G.
474,608	Electro-Metallurgical Research Co., Ltd. (*in liquidation*) and S. Wernick.
474,609	Electro-Metallurgical Research Co., Ltd.
474,704	F. A. Wales.
475,065	General Electric Co., Ltd., and F. C. Mayes.
476,161	Electro-Metallurgical Research Co., Ltd.

477,286	W. K. Wilson, F. H. Thomas and de Havilland Aircraft Co.
479,220	G. D. Skinner and Benjamin Electric, Ltd.
479,225	General Electric Co., Ltd.
479,401	British Thomson-Houston Co.
479,665	Siemens and Halske A.-G.
481,252	H. Wolff.
482,563	A. G. Chaybany.
483,776	S. R. Sheppard.
483,798	Magnesium Elektron, Ltd.
483,988	Aluminium Protection Co., Ltd.
484,492	Vereinigte Aluminium-Werke.
485,114	F. Kleeman.
487,406	I. G. Farbenindustrie A.-G.
487,605	F. Hill and J. A. Radley.
488,441	Schweizerische Lokomotiv- und Maschinenfabrik.
488,952	F. Hill and J. A. Radley.
489,169	Aluminum Co. of America.
489,220	C. H. R. Gower and E. Windsor-Bowen.
489,757	O. Vieli.
489,926	K. Nagata.
491,618	M. Schenk.
491,974	Aluminum Colors, Inc.
492,345	Aluminum Colors, Inc.
492,838	Y. Yasoshima.
494,054	E. Potter.
494,376	Vereinigte Aluminium-Werke.
494,426	Aluminium-Industrie A.-G.
494,501	C. Lorenz A.-G.
496,436	H. Hongo.
497,525	L. Marx.
497,648	Aluminum Colors, Inc.
499,643	P. King-Morgan.
500,115	P. King-Morgan.
500,930	Vereinigte Aluminium-Werke A.-G.
501,470	Fabrik Leonischer Waren Benedict and Dannheisser G.m.b.H.
502,278	General Motors Corporation.
502,957	K. Nagata.
503,451	L. T. Gmach.
504,216	Magnesium Elektron, Ltd.
508,723	Magnesium Elektron, Ltd.
511,922	Peintal S.A.
513,149	P. King-Morgan.
513,530	British Aluminium Co., Ltd., and A. N. D. Pullen.

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